

# BIOGEOCHEMICAL PROCESSES AFFECTING THE FATE OF DISCHARGED DEEPWATER HORIZON GAS AND OIL

NEW INSIGHTS AND REMAINING GAPS IN OUR UNDERSTANDING

By John W. Farrington, Edward B. Overton, and Uta Passow

A large oil slick floats atop the surface of the turquoise waters of the Gulf of Mexico about 1.5 km south of Perdido Key, Florida, on June 12, 2010, nearly two months after the Deepwater Horizon drilling rig explosion. Photo credit: Petty Officer 1<sup>st</sup> Class Tasha Tully

**ABSTRACT.** Research funded under the Gulf of Mexico Research Initiative provided new insights into the biogeochemical processes influencing the fate of petroleum chemicals entering the Gulf of Mexico from the Deepwater Horizon (DWH) accident. This overview of that work is based on detailed recent reviews of aspects of the biogeochemistry as well as on activities supported by the US Natural Resource Damage Assessment. The main topics presented here are distribution of hydrocarbons in the water column; the role of photo-oxidation of petroleum compounds at the air-sea interface; the role of particulates in the fate of the DWH hydrocarbons, especially marine oil snow (MOS) and marine oil snow sedimentation and flocculent accumulation (MOSSFA); oil deposition and accumulation in sediments; and fate of oil on beaches and in marshes. A brief discussion of bioaccumulation is also included. Microbial degradation is addressed in a separate paper in this special issue of *Oceanography*. Important future research recommendations include: conduct a more robust assessment of the mass balance of various chemical groupings and even individual chemicals during specific time intervals; seek a better understanding of the roles of photo-oxidation products, MOS, and MOSSFA and their relationships to microbial degradation; and determine the fates of the insoluble highly degraded and viscous oil residues in the environment.

## INTRODUCTION

This article provides an up-to-date overview of some of the important research findings of the past five years related to the biogeochemical processes influencing the immediate (minutes to months) and longer-term (years to a decade or longer) fate of chemical constituents from the Deepwater Horizon (DWH)–Macondo accident that took place April 20, 2010. Our intention is to guide general ocean science researchers and marine policy and management practitioners through the highlights of research funded by the Gulf of Mexico Research Initiative (GoMRI) and the US Natural Resources Damage Assessment (NRDA), although we hope this overview will be helpful to oil research specialists as well. Specifically, this article updates the informative 2016 papers by Passow and Hetland, Passow and Ziervogel, and Tarr et al. in the last GoMRI special issue of *Oceanography*. Our effort here is informed by the more detailed, recent reviews that provide a holistic accounting of the biogeochemistry and fate of the DWH gas and oil chemicals (Burd et al., 2020; Kostka et al., 2020; Kujawinski et al., 2020; Quigg et al., 2020; Ward and Overton, 2020; Passow and Overton, 2021, and recent work of authors Edward Overton and Uta Passow). While our effort focuses primarily on GoMRI-funded research, it also

attempts to place that research, where appropriate, within a wider context of other DWH-related research and assessments such as the NRDA activities, which were published in the peer-reviewed scientific literature after the settlement of the NRDA case in the US federal courts.

It is not possible in this synopsis to cite, present, and discuss all the relevant research pertaining to the fates of gas and oil hydrocarbons connected with the DWH accident. The relevant literature is voluminous. More than 400 papers have been published on GoMRI-funded research, all focusing in some measure on the fate of Deepwater Horizon gas and oil under the category fates/biogeochemistry (see <https://research.gulfresearchinitiative.org/gomri-publications/>). Our apologies to those researchers whose important papers are not cited and discussed.

The major areas of research in need of updating include: (1) water column hydrocarbon measurements during and after the spill; (2) photo-oxidation of oil compounds and their water versus oil solubilities; (3) marine oil snow (MOS), marine oil snow sedimentation and flocculent accumulation (MOSSFA), and oil-mineral aggregates (OMAs); (4) long-term fate of oil deposited in deep-sea sediments (aerobic and anaerobic); (5) fate of oil stranded on beaches (mostly aerobic);

(6) oil that came ashore in marsh areas (aerobic and anaerobic); and (7) microbial degradation of DWH oil chemicals. Microbial degradation will only be briefly raised because there is a very informative discussion in this issue by Weiman et al. about microbiology from the perspective of genomics/proteomics, ecology, and ecosystems.

First, we will set the scene with a brief history of oil pollution in the Gulf of Mexico.

“But regardless of any alleged toxicity to oysters, two facts should be borne in mind. First, oil is quickly taken up by oysters, imparting an oily taste to the flesh which renders the meat unsalable. Second, the effect of oil pollution will last over a long period, for oil is carried to the bottom by suspended mud particles and released from time to time by storms, tonging, or dredging.”

— Galstoff et al. (1935)

The quote and the paper/report from which it is drawn introduces the long history of oil pollution fates and effects studies in the Gulf of Mexico coastal areas that progressively moved to deeper waters as oil and gas exploration and production moved offshore to the continental shelf (e.g., NRC, 1985, 1993; Transportation Research Board and National Research Council, 2003; Boesch and Rabalais, 1987). The quote also highlights two aspects, among the many now known, of the fates of oil discharged to the marine environment: (1) bioavailability to various organisms and their food webs, and back to humans, and (2) the role of particulate matter in deposition to sediments, resuspension, and the longer-term fate of oil chemicals in various types of sediments.

Fortunately, much illuminating research has been conducted worldwide since the Galstoff et al. (1935) pioneering report. The variety of physical transport and biogeochemical processes acting on the gas and oil chemicals and their



fates after discharge to the environment has been the subject of research over the past several decades (e.g., see NRC, 1975, 1985, 1999; Transportation Research Board and National Research Council, 2003; Royal Society, 1980; K. Lee et al., 2015, among several others).

Our understanding of the fate of gas and oil inputs to the marine environment has evolved within the framework of progress in understanding the biogeochemistry of natural biosynthesized organic matter in the marine environment and all human-mobilized and synthesized organic chemicals of environmental concern (e.g., Bianchi and Canuel, 2011; Farrington and Takada, 2014; Wakeham and Canuel, 2016; Takada and Karapanagioti, 2019; Wakeham and Lee, 2019; Steen et al., 2020). Fundamental physical chemistry and aquatic chemistry principles and examples for a variety of organic chemicals, including a range of hydrocarbon types and molecular weights found in the DWH gas and oil, are presented and discussed in the comprehensive textbook by Schwartzenbach et al. (2017).

Rullkötter and Farrington (2021, in this issue) review and briefly describe the complex compositions of petroleum and petroleum products in general and specifically of the DWH oil. Boufadel et al. (2021, in this issue) describe the influence of various physical processes within many temporal and spatial scales on the gas and oil discharged at the broken well riser as well as on the resulting surface oil slick. The interaction of the chemical composition with physical, chemical, and biological processes cannot be compartmentalized in a neat manner and to try and do so is to oversimplify a very complex situation.

## **OIL HYDROCARBONS IN THE NORTHERN GULF OF MEXICO ECOSYSTEMS PRIOR TO THE DWH SPILL**

The Galstoff et al. (1935) quote notes the initial years of a continuing history of chronic human-caused petroleum inputs

to the nearshore areas of the northern Gulf of Mexico. As noted by several assessments, there are numerous natural oil seeps in the Gulf and in several other areas worldwide (e.g., Transportation Research Board and National Research Council, 2003; MacDonald et al., 2015; Kennicutt, 2017). As a generalization, these seeps, estimated to leak in excess of 42 million gallons (160 million liters) annually, have been ongoing for thousands of years or more, and some discharges can be episodic (Kennicutt, 2017, and references therein). It is reasonable to expect, as noted in Weiman et al. (2021, in this issue), that microbial communities in and around natural seeps have evolved or developed to take advantage of the leaking gas and oil hydrocarbons as a source of carbon and metabolic energy.

Assessments of fossil fuel hydrocarbon compounds in northern Gulf of Mexico sediments and some benthic organisms were made as part of a Deep Gulf of Mexico Benthos Program from 2000 to 2002: “The purpose was to provide a better understanding of how oil and gas exploration and production might affect the ecosystem and its natural inhabitants” (Rowe and Kennicutt, 2008; Kennicutt, 2017). Sample analyses and data interpretation for the potentially toxic polycyclic aromatic hydrocarbons (PAHs) in surface sediments (Wade et al., 2008) and a population of amphipods (Soliman and Wade, 2008) were part of this effort. We note this as one example of studies of fossil fuel hydrocarbons in northern Gulf of Mexico ecosystems prior to the DWH accident.

In addition to chronic inputs from land sources and offshore platforms, there have been numerous small and medium size spills in the coastal areas of the Gulf (Transportation Research Board and National Research Council, 2003). As with many developed and industrialized coastal areas, there are numerous oil processing, refining, and storage facilities in those coastal areas. Severe storms inundate some of these areas and

cause spillage of various amounts of oil. For example, in 2005 during Hurricane Katrina, oil spilled into the Louisiana coastal area from various facilities (e.g., Pine, 2006). A baseline of petrochemical pollution in coastal Louisiana assembled from 3,240 surface sediment samples by Iqbal et al. (2007) provides one view of the influence of the various inputs discussed above.

Another example of oil inputs is the leakage that has resulted from the toppling of Taylor Energy’s Mississippi Canyon Block 20 site production platform following a regional upslope seafloor failure on September 15, 2004, caused by Hurricane Ivan. This slow, variable leakage of inputs predates DWH, is still in progress, and has attracted more attention in the past few years (Bryant et al., 2020).

Some individual chemicals in the group of aromatic hydrocarbons, particularly PAHs, are of concern from the perspective of effects on organisms and also on human health (NRC, 1985; Transportation Research Board and National Research Council, 2003; Dickey and Huettel, 2016; Farrington, 2020a). Petroleum is not the only source of many of these PAHs. Combustion of fossil fuels and wood for energy, and natural grass and forest fires, all contribute these types of compounds to the environment (e.g., see Lima et al., 2005).

Adding to the issue of biogenic/early diagenesis sources for low concentrations of PAHs, it has been known for many decades that marine organisms biosynthesize a limited number of *n*-alkanes and *n*-alkenes as well as highly branched alkanes and transform the phytol portion of the chlorophyll molecule to pristane. Basking sharks accumulate squalene in their livers (e.g., NRC, 1985; Valentine and Reddy, 2015, and references therein). Notably, Lea-Smith et al (2015) reported pentadecane, heptadecane, and 8-heptadecane biosynthesis by *Prochlorococcus* and *Synechococcus* (depending on the strain cultured), the most abundant marine cyanobacteria. The authors cal-

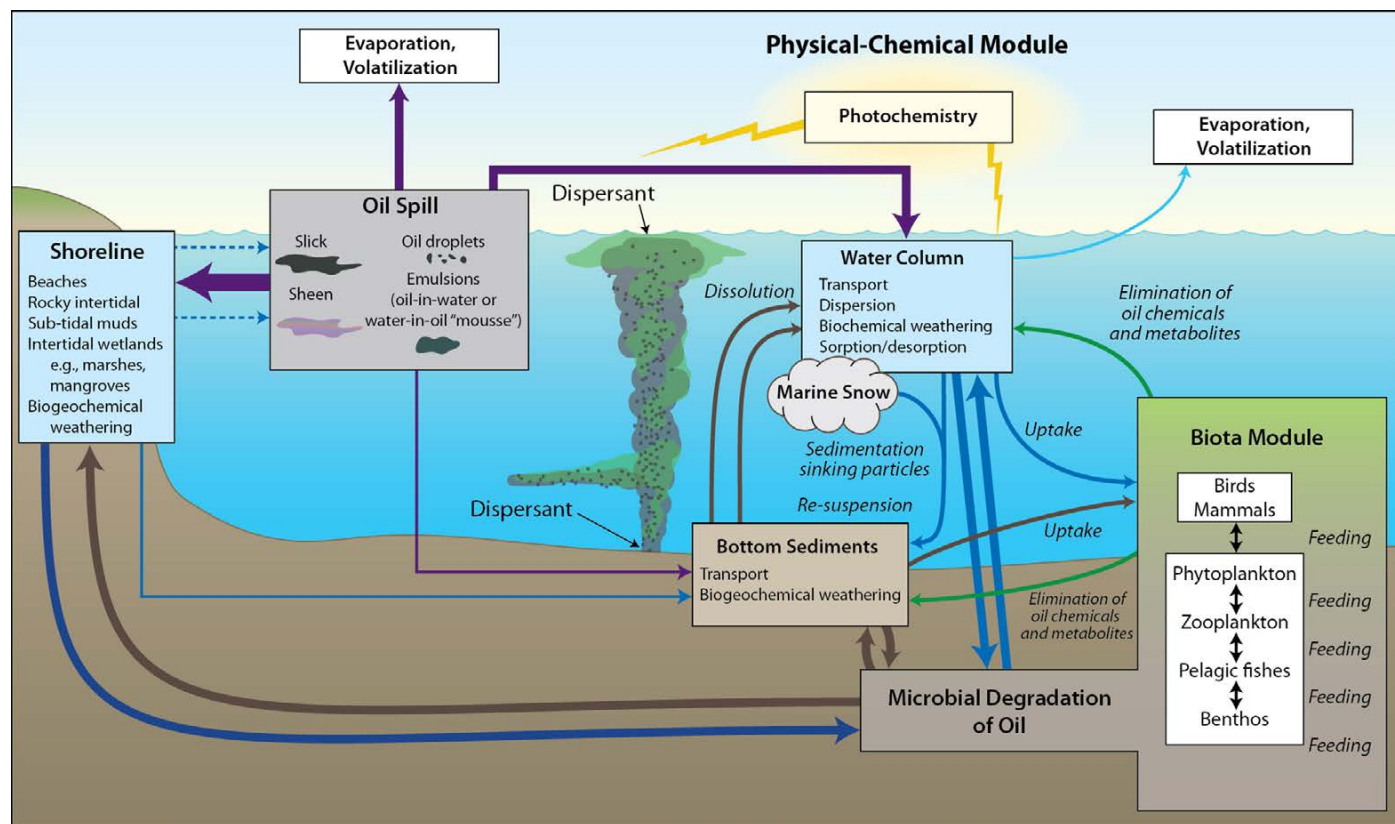
culated that this results in a biosynthesis each year of between 269 and 539 million metric tons of these hydrocarbons for *Prochlorococcus*, and between 39 and 232 million metric tons of these hydrocarbons for *Synechococcus* for the world ocean. This synthesis has important implications for the potential long-term presence of bacteria capable of degrading *n*-alkanes in the marine environment (Weiman et al., 2021, in this issue), and this biosynthesis adds to the biogenic/methanogenic production of methane from biological and diagenetic processes (Reeburgh, 2007).

Thus, when tracking the fate of the DWH spilled oil, it has been important to be cognizant of the other sources of hydrocarbon/oil inputs to the same Gulf of Mexico area and to use analytical methods and interpretation of data that can successfully distinguish inputs from the spill, especially over longer periods of time and at low concentrations. It can be helpful to identify the specific

chemical composition of the DWH oil and the relative compositions of specific structures of molecules known as petroleum biomarkers (molecular biomarkers to some organic geochemists—different from what are now commonly considered biomarkers in molecular biology; Rullkötter and Farrington, 2021, in this issue, and references therein). The ratios of these petroleum biomarkers to other chemicals in DWH oil, such as the alkylated PAH homologues, become important in distinguishing the presence of DWH oil from other oil sources as well as from other aliphatic hydrocarbons and PAH sources. The papers referenced in Stout and Wang (2018) provide a thorough discussion, with several examples that include some from the DWH spill. Boehm et al. (2018) provide a recent assessment of the difficulties encountered in and the limitations of the application of ratios of PAHs in terms of identifying initial sources of some, most, or all of the PAHs in given samples.

## IMPORTANT FACTORS TO CONSIDER REGARDING THE RELATIONSHIP BETWEEN THE CHEMICAL COMPOSITIONS OF DWH GAS AND OIL AND THEIR BIOGEOCHEMISTRY FATES

Figure 1 depicts the biogeochemical fates of gas and oil; key biogeochemical processes are listed in Box 1. Another diagram of the environmental weathering of crude oil that has proved helpful is Figure 1 in Tarr et al. (2016), in the earlier *Oceanography* special issue about GoMRI research. These figures are both simplified schematics of a complex set of interacting processes. Some of the important processes have been the subjects of reasonably robust numerical modeling efforts in recent years as discussed in Boufadel et al. (2021) and Westerholm et al. (2021), both in this issue. One key point to reemphasize here is that a complex mixture of chemicals with a wide range of molecular weights and specific chemical structures (see Rullkötter and Farrington, 2021, in



**FIGURE 1.** Schematic summarizing the fate of Deepwater Horizon gas and oil, including physical-chemical and biological modules with relevant processes. From Farrington et al. (2016)

## Box 1. Key Biogeochemical Processes Controlling the Fate of DWH Gas and Oil Inputs

*Not in temporal order or order of importance.*

- Gas-oil-water partitioning and dissolution
- Gas-oil-water to atmosphere volatilization
- Water-oil emulsification
- Photo-oxidation at sea surface and on shorelines/beaches
- Sorption/desorption to/from particulates of various types, including transparent extracellular polymer and marine snow particles
- Emulsion formation at the sea surface, mainly water-in-oil emulsions
- Oil stimulation/instigation of formation of transparent extracellular polymer leading to more marine snow formation
- Aggregation and disaggregation of particulate matter
- Deposition of particulate matter with associated oil chemicals to sediments
- Resuspension of recently deposited material, transport, and redeposition
- Microbial degradation during all of the above
- Uptake by marine organisms, metabolism, excretion, food web transfer of oil compounds and/or metabolites

Note that the importance of any of these processes for any gas or oil group of compounds or individual compound is a function of their molecular weights and chemical structures because they govern solubility, vapor pressure, sorption/desorption, microbial degradation, and uptake/metabolism/excretion/food web transfer by marine organisms.

this issue) move through the pathways outlined in [Figure 1](#).

Passow and Overton (2021) succeeded in constructing an estimated rough mass balance budget for the released oil and gas as a whole, even though the effort was complex. Based on the literature they consulted regarding the total input of gas and oil and post-spill field measurements in various places by numerous assessments and research efforts, they found that about 25% was recovered, 5%–15% was burned (volatile organics and oil in the surface slick), and 60%–70% was spread and weathered within the Gulf of Mexico. It was impossible to accurately budget the individual weathering processes that included: dilution in the water column (soluble, low molecular weight compounds and dissolved organic matter), volatilization and aerosol formation of some of the compounds to the atmosphere, photo-oxidation and oil/water solubility of photo products, sorption to and incorporation into particles and deposition to sediments, microbial degradation in the water column and sediments, and stranding ashore on beaches and marshes (see Tarr et al., 2016, for a very helpful and concise discussion of weathering of oil).

In this context, it is important to remember that in the strictest sense, each individual chemical within DWH gas and oil has its own mass balance, that is, its own relative distribution among various compartments in the environment (air, oil, dissolved in water, particulates in water, sediments, and biota). Thus, not all areas or ecosystems in the northern Gulf of Mexico were contaminated by all compounds of the crude oil. For example, oil reaching shorelines was largely weathered by photo-oxidation and removal of volatile compounds. Certain compounds, less susceptible to weathering, accumulated in various ecosystems (e.g., on shorelines, at the seafloor), reaching concentrations above background or detectable levels for varying periods of time. These compounds included some of the chemicals, such as PAHs of concern for known or potentially adverse effects, as discussed in other papers in this issue (Rullkötter and Farrington. 2021; Murawski et al., 2021; Halanynch et al., 2021).

There are two other points worth mentioning. First, several of the papers concerning the fate of DWH oil in fact describe the analyses of oil *residues*. In those papers, the term “oil” does not refer to the crude oil at the time of discharge, but rather it means the portion of original oil chemicals that remain in the sample at the location and time of sample collection. Weathering/biogeochemical processes continuously alter the composition of oil in the environment. We make this point, because the term “residue” could be interpreted by some to mean a minor or trace amount, although chemists use the term to refer to the altered state of the spilled oil, which may be present in some samples at very high concentrations. The key is to assess the actual concentrations of specific hydrocarbons.

Second, another term found in the relevant scientific literature we cite is *target analytes*. Petroleum, or oil such as that in the DWH spill, is composed of many thousands of individual chemicals. In many cases, there has been agreement to analyze quantitatively a subset of important and abundant hydrocarbons as being representative of those compounds of greatest concern in the composition of the whole oil. In fact, many analyses report no more than 200 individual petroleum compounds. These target analyte compounds are also those for which there are well-established analytical methods and whose qualitative identifications and quantitative detection limits have been verified by the use of Standard Reference Materials from the US National Institute of Standards and Technology (or other similar agencies worldwide) and by the analysis of round robin quality assurance/quality control samples.



For example, a set of specific alkanes and specific aromatic hydrocarbons are measured frequently, usually identified in tables presented as supplementary materials, and reported as total concentrations of target analytes in the main body of a paper. Typical target analytes include normal alkanes (*n*-alkanes from C<sub>10</sub> to C<sub>30</sub> or C<sub>40</sub>), pristane, phytane, two- to six-ringed PAH compounds and their alkyl homologues, and the “petroleum biomarkers” hopanes, steranes, and tri-aromatic diagenetic steroid compounds.

Compared to analyses from earlier decades, significant achievements have been possible using these methodological advancements. However, as noted in Rullkötter and Farrington (2021, in this issue), analytical chemistry methodology has advanced to the point where quantitative data on as many as a thousand or more oil chemicals is feasible, although expensive, and may become routine in the not-too-distant future. Thus, in many cases there has been agreement to analyze a subset, for example, a set of PAHs, and on occasion report the total of that subset as the concentration of the “target PAH analytes,” or total target PAHs, as opposed to “total PAHs.” The latter term implies that it includes analysis of all PAHs in the sample.

## SHORTER-TERM FATE: WATER COLUMN PROCESSES

The dynamic processes of importance for the fate of the gas and oil are: (1) initial gas-oil-water partitioning between gas and oil bubbles and water in the water column; (2) progressive partitioning over time between oil in slicks at the surface, in the water column, and in air; (3) stranding on shorelines; and (4) deposition to sediments. A review of the physics and physical chemistry of these processes by Socolofsky et al. (2016) is updated by Boufadel et al. (2021, in this issue). There was a paucity of actual measurements of petroleum chemicals in the immediate vicinity of the well site and the vertical plume in the earlier days of the spill due to ongoing spill response activities and

safety concerns. Thus, a more detailed scientific understanding, as presented and discussed in Socolofsky et al. (2016) and Boufadel et al. (2021, in this issue), is dependent on the interaction of various scaled laboratory experiments and modeling exercises that incorporate fundamental principles. Note that compounds in their gaseous phase form bubbles, whereas the term droplets refers to liquid oil compounds. Oil droplets in water are sometimes also referred to as particles or particulate oil because they are retained on filters. When released at depth and under high pressure, compounds that are gaseous at atmospheric pressure may be liquid and thus shift from their liquid to their gaseous phase during their ascent.

Oil entering the bottom waters from the DWH well was observed visually as a cloud of seawater containing mixtures of natural gas and oil droplets of various sizes, combined with brine from the well, resulting in a complex, uneven, interwoven brownish, tan, and yellowish plume (see image in Figure 5 of McNutt et al., 2012). At times, when drilling mud was being injected to attempt to reduce or stop the flow, an admixture of drilling mud became part of the plume. There were also reports that some gas hydrates formed, which is consistent with the temperatures and pressures of the bottom waters receiving the release. The public was treated for a period of time to live video camera feeds shown on various TV news outlets and web-based sources (authors’ personal observations).

The separation of hydrocarbon gases from oil occurred prior to or shortly after exit from the broken riser pipe and broken blowout preventer (as noted in Boufadel et al., 2021, in this issue); as the gases separated from oil and began to rise through the water column, the water-soluble gas components such as methane, ethane, and propane dissolved into surrounding waters. The vertical plume transported gas and oil chemicals to surface waters from about 1,500 m depth. During that process, gas bubbles dissolved, oil droplets became smaller, and the more soluble

components of the oil went into solution, with partitioning between the oil droplets and the surrounding seawater despite the old adage that oil and water do not mix. **Table 1** illustrates the range of PAH solubilities, which span several orders of magnitude and are but one illustration of the range of physical-chemical parameters of individual chemicals that constitute gas and oil.

Ji et al. (2020) provide a detailed review of formation, detection, and modeling of the DWH submerged oil. In addition to the vertical plume, a significant horizontal plume, centered about 1,100 m depth, also evolved in the water column, and there were several smaller plumes at intermediate depths (Ji et al., 2020; Boufadel et al., 2021, in this issue). Modeling estimates and observations note the extent of the horizontal plume (often designated as the deep intrusion layer) to be 200 km to 400 km to the southwest and at other times in varying directions such as the northeast, depending on the variable

**TABLE 1.** Solubility of some aromatic/polycyclic aromatic hydrocarbons. From Table 4.3 in Transportation Research Board and National Research Council (2003), showing examples taken from the much larger data set by MacKay et al. (1992).

COMPOUND	MOLECULAR WEIGHT (Daltons)	SOLUBILITY (mg L <sup>-1</sup> )
Benzene	78	1,700
Toluene	92	530
Ethylbenzene	106	170
p-Xylene	120	150
Naphthalene	128	30
1-Methylnaphthalene	142	28
1,3-Dimethylnaphthalene	156	8
1,3,6-Trimethylnaphthalene	170	2
Phenanthrene	178	1
Fluorene	202	2
Dibenzo-thiophene	184	1.1
Chrysene	228	0.002

water circulation processes (e.g., Ji et al., 2020; Passow and Overton, 2021). Early observation using UV-fluorescent colored dissolved organic matter measurements clearly indicated some type of horizontal plume; detector responses were consistent with its being composed of oil droplets and dissolved PAH. A few more detailed water samples were extracted and analyzed for PAHs by laboratory-based gas chromatography-mass spectrometry (Diercks et al., 2010). Within a few weeks after the Diercks et al. cruise, Camilli et al. (2010) used both UV-fluorescence and an innovative, novel, in situ mass spectrometer mounted on the autonomous underwater vehicle *Sentry*. Additional samples collected using a water column rosette were analyzed in order to define the horizontal plume. A less pronounced plume

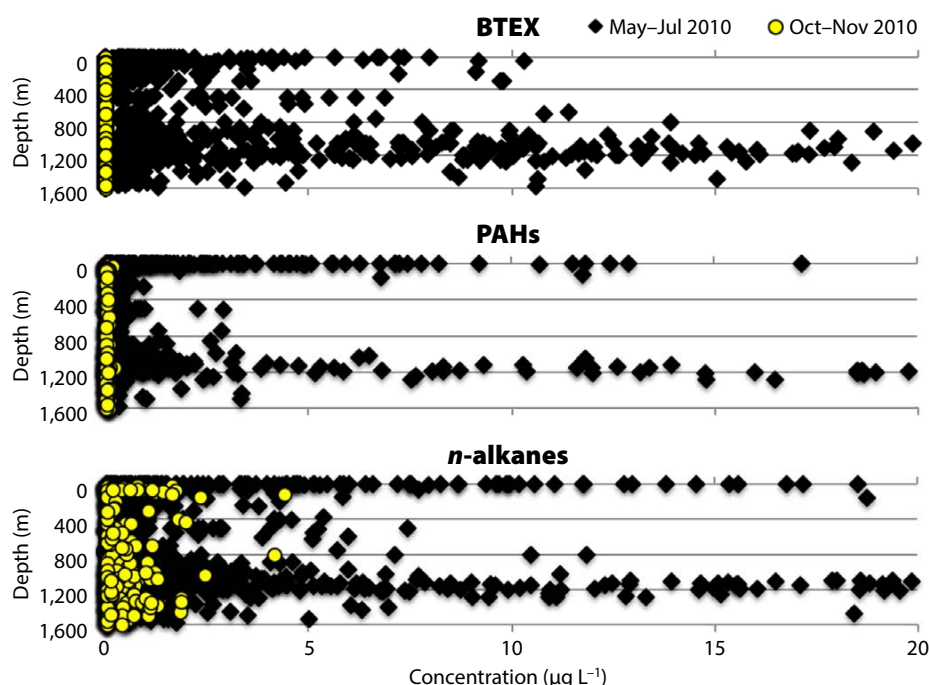
signal was detected to the northeast of the well site during the same research cruises by the same authors. The chemicals they measured included the gases methane ( $C_1$ ) to butane ( $C_4$ ) and the low molecular weight liquids benzene, toluene, and xylenes. The plume to the northeast “collided” at times with the continental slope, in some areas resulting in oil chemicals contaminating surface sediments (e.g., Passow and Overton, 2021, and references therein). There were indications at various times, as noted in the above-mentioned references, of other smaller horizontal plumes.

A few years later, a master’s thesis (Watson et al., 2013; Watson, 2014) and detailed PAH data published by Boehm et al. (2016) evaluated results from gas chromatography and GC-mass

spectrometry measurements of a large number of water samples from the vicinity of the well site collected as part of the US government and BP NRDA effort. **Figure 2** replots data from Watson (2014), which compares data for BTEX (benzene, toluene, ethylbenzene, and xylenes) concentrations, total of the target PAHs, and total of target alkanes. Payne and Driskell (2018) discuss the difficulties in sampling, quality control, and quality assurance, and the challenges of sampling truly dissolved compounds, compounds in oil droplets or associated with particulates for PAHs, or other hydrocarbons.

The processes that control the water column distributions of oil compounds in time and space include complicated gas and oil bubble dynamics within turbulent flow, as well as horizontal and vertical flow and mixing (see Boufadel et al., 2021, in this issue). These processes result in the dilution of the input, potentially in microbial degradation of gas and oil hydrocarbons (Weiman et al., 2021, in this issue), and in sorption-desorption to various particles in the water column. Association with particles may be followed by biodegradation, ingestion, or deposition, and after deposition, continuing biodegradation and/or resuspension and redeposition.

If there were an ideal, soluble, non-biodegradable gas or oil compound that did not partition with particles, we might expect it to behave and dilute as did the  $CF_3SF_3$  tracer introduced to the deep Gulf of Mexico to study physical dynamics processes of the water column (Ledwell et al., 2016). Of course, there is no such ideal inert and soluble gas or oil chemical in petroleum. In addition, the DWH input lasted longer than one day, was composed of multiphase gas and oil comprising thousands of chemicals, and was greater on amount and spatial extent than the tracer. Nevertheless, the tracer experiment does provide important insights. As Ledwell et al. (2016) explain, the dilution is not uniform in time and space; mixing was much more rapid in the continental slope region compared to the deeper



**FIGURE 2.** Concentration profiles for all water samples collected within 50 km of the wellhead where the water depth was  $\geq 1,000$  m. BTEX = benzene, toluene, ethylbenzene, and xylenes. PAHs = polycyclic aromatic hydrocarbons. Total PAH concentrations were the sum of the following 44 PAHs: naphthalene, C1-naphthalenes, C2-naphthalenes, C3-naphthalenes, C4-naphthalenes, acenaphthylene, acenaphthene, fluorene, C1-fluorenes, C2-fluorenes, C3-fluorenes, anthracene, phenanthrene, C1-phenanthrenes/anthracenes, C2-phenanthrenes/anthracenes, C3-phenanthrenes/anthracenes, C4-phenanthrenes/anthracenes, dibenzothiophene, C1-dibenzothiophenes, C2-dibenzothiophenes, C3-dibenzothiophenes, C4-dibenzothiophenes, benzo(b)fluorene, fluoranthene, pyrene, C1-fluoranthenes/pyrenes, C2-fluoranthenes/pyrenes, C3-fluoranthenes/pyrenes, C4-fluoranthenes/pyrenes, benzo(a)anthracene, chrysene, C1-chrysenes, C2-chrysenes, C3-chrysenes, C4-chrysenes, benzo(b)-fluoranthene, benzo(j+k)fluoranthene, benzo(a)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. The compounds used to measure total *n*-alkane\* concentrations were C9-40, pristane, phytane, 2,6,10 trimethyldodecane, 2,6,10 trimethyltridecane, and norpristane. (\*The correct term is total designated alkanes). Replotted from Watson (2014) with permission

interior waters of the Gulf. Maximum concentrations of the tracer found in their surveys were measured at dilutions of  $10^4$ ,  $10^7$ , and  $10^8$  at one-week, four-month, and 12-month survey times, respectively.

It is clear from the sampling and analyses reported that there was a period of significant contributions of DWH gas and oil to the nearby deep waters of the Gulf of Mexico and in the immediate region of the Macondo well site. Once the well was capped, the concentrations in the water column rapidly diminished to below detection limits in areas sampled. However, the elevated concentrations of DWH oil compounds collected in sediment traps many months after the capping of the well demonstrated that DWH oil was still present in the water column (Giering et al., 2018; Passow and Stout, 2020). Weiman et al. (2021, in this issue) describe microbial processes that were involved in biodegradation of the DWH oil, and Murawski et al. (2021, in this issue) discuss what biological effects may have ensued due to the period of elevated concentrations in the water column.

Concentrations of petroleum hydrocarbons with clear DWH molecular characteristics spread into continental shelf surface and then bottom waters off Louisiana (Turner et al., 2019; see Figure 3 for sampling locations). Sampling began in May 2010 and continued initially once a month, and at greater intervals later. Turner et al. present field observations and logical inference that the initial May 2010 samples were already influenced by DWH spilled oil. Concentrations increased markedly from May through June, July, August, and September of 2010, decreased relatively rapidly until 2015, and then continued to decrease slowly from July 2015 through 2019. Data for the total target analyte aromatic hydrocarbons in the water showed  $153 \mu\text{g L}^{-1}$  in August 2010 and an increase to  $323 \mu\text{g L}^{-1}$  in September 2010, followed by a decrease over time until 2018 when concentrations were in the range of  $0.01 \mu\text{g L}^{-1}$ . The water samples contained a higher proportion of three-ring aromatic compounds

(e.g., phenanthrene and alkyl phenanthrenes) than the initial DWH oil, which had a higher proportion of lower molecular weight aromatic compounds (e.g., the two-ring aromatic hydrocarbon naphthalene and alkylnaphthalenes). It is likely that a combination of volatilization, dissolution from the droplets, and biodegradation of some of the naphthalene and alkyl naphthalenes occurred during transport from the DWH site to the sampling location. Data for the adjacent inshore marsh areas are discussed in a later section.

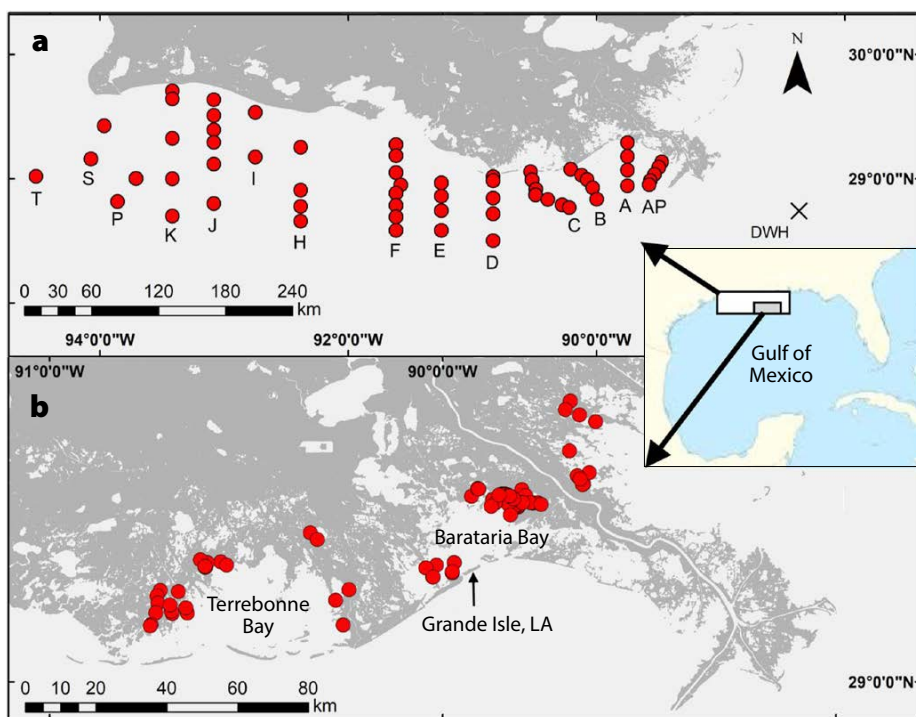
### FATE OF OIL AT THE AIR-SEA INTERFACE: THE IMPORTANCE OF PHOTO-OXIDATION

Substantial amounts of oil rose to the sea surface and formed oil slicks and sheens. In short order, the more volatile components of the surfaced oil evaporated. Mixing due to wind and waves promoted formation of a water-in-oil emulsion that exhibited many bright to creamy colors (e.g., orange). These emulsions, termed “mousse” years ago because of their resemblance to the dessert chocolate mousse (e.g., NRC, 1985), have been

reported as important and studied extensively with previous oil spills.

Photo-oxidation of oil at the sea surface had been recognized for decades, as noted by reviews in Payne and Philips (1995), Ward and Overton (2020), and Ward et al. (2020). Although the Transportation Research Board and National Research Council (2003) report stated that “photo oxidation is unimportant from a mass balance consideration,” we can find no substantive discussion or references that support this statement. That same 2003 report acknowledged that products of photo-oxidation of oil chemicals can produce toxic reaction products of concern for both immediate and longer-term impacts. There was also recognition that photo-oxidation is an important process in the fates of oil chemicals evaporated from oil slicks into the atmosphere.

Research focused on the DWH oil spill provided important results that require revision of the assertion from the Transportation Research Board and National Research Council (2003) report, at least for oils spilled in tropical



**FIGURE 3.** Gulf of Mexico sampling locations in (a) offshore waters, and (b) marsh sediments. The Deepwater Horizon (DWH) site is indicated by the X in (a). Reproduced from Turner et al. (2019) with permission



and subtropical regions, or at higher latitudes during the summer. The results of a GoMRI-funded synthesis workshop focused on photochemistry and photo-oxidation are summarized in Ward and Overton (2020). The meshing of results from field observations and field sample analyses, laboratory-scale flasks experiments, and mesocosm experiments has been key to significant progress in our knowledge about photo-oxidation associated with surface oil slicks. In reviewing all of this research, Ward and Overton (2020) and Ward et al. (2020) provide an interesting comparison of the relative importance ascribed to photo-oxidation

compared to other oil slick weathering processes (evaporation, emulsification, and biodegradation) pre- and post-DWH research (Figure 4a).

Numerous experiments and analyses of field samples have tied photo-oxidation to known photochemistry reactions. These include both direct and indirect photochemical reactions, as discussed by Ward and Overton (2020). Their Figure 5 incorporated here as Figure 4b is a simplified representation of both direct and indirect photo-oxidation. Many, if not most, of these findings would not have been possible without the utilization of new analytical chemistry methods, as discussed in

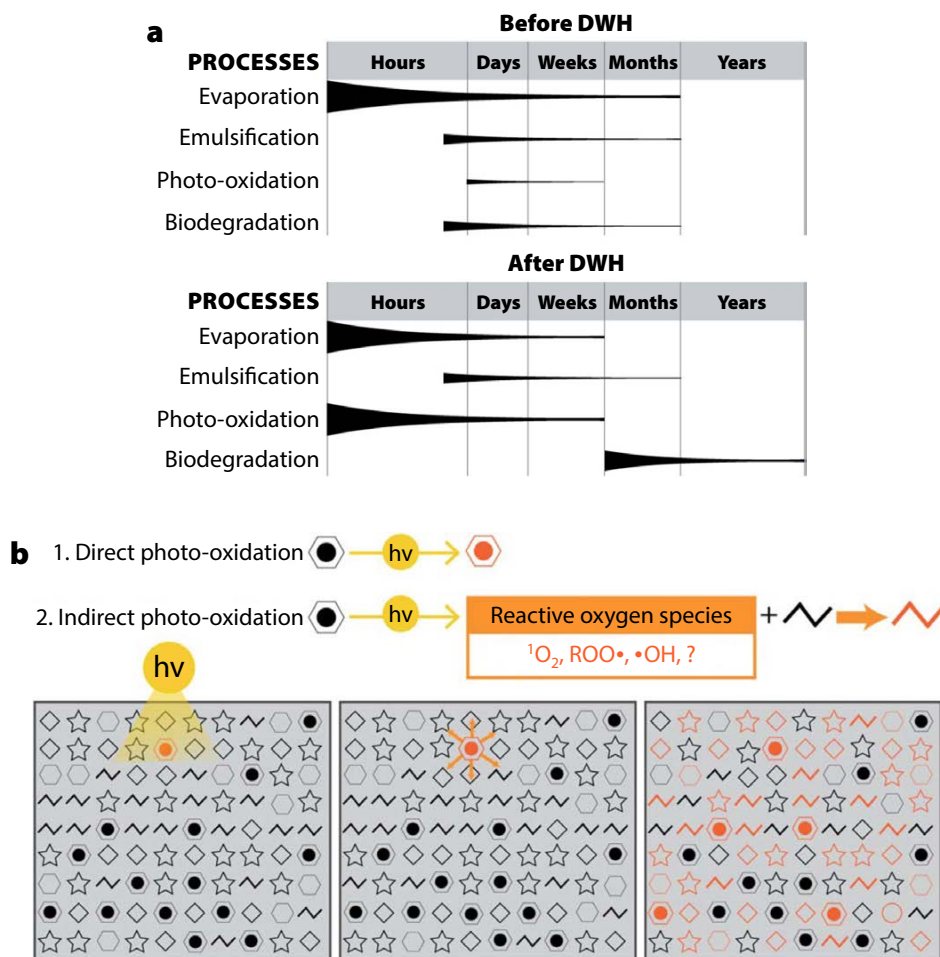
Rullkötter and Farrington (2021, in this issue). In particular, analyses by ultra-high-resolution FT-ICR-MS (Fourier transform-ion cyclotron resonance-mass spectrometry) have provided extensive data that challenge our ability to identify the myriad reaction pathways and chemical structures of thousands of photo-oxidation-induced reaction products (Rullkötter and Farrington, 2021, in this issue).

Ward and Overton (2020) note an additional important aspect of these findings: the technological advances in remote sensing that allow acquisition of information on oil film extent and thickness (MacDonald et al., 2015) permit photochemical rate modeling to be applied to the DWH spill. However, even better quantitation of film thickness over space and time is needed to improve the models designed to estimate the extent of photochemical/photo-oxidation reactions in any given oil spill.

Already, these new findings have allowed photo-oxidation/photochemistry to be incorporated in conceptual models to reflect more accurately the role photo-oxidation plays in the fate of oil at the sea surface or in surface waters (NASSEM, 2020). Results from this work have important implications for response to oil spills. For example, Ward et al. (2018) discuss how photochemical oxidation of oil changes the oil's solubility in dispersant solvent, which has the potential to reduce the effectiveness of aerial dispersant application.

A brief summation of the three key findings as set forth by Ward and Overton (2020) are as follows (quoting the initial sentences):

1. "The rate and extent of photochemical weathering was much greater for DWH surface oil than expected based on early conceptual models of oil weathering."
2. "Indirect photochemical processes played a major role in the partial oxidation of the floating surface oil."
3. "The extensive and rapid changes to the physical and chemical properties



**FIGURE 4.** (a) The relative importance of floating surface oil weathering processes as understood prior to and after the Deepwater Horizon spill of 2010. (b) A conceptual model depicting direct and indirect photo-oxidation. In direct photo-oxidation (left panel), a light-absorbing molecule (depicted as a black aromatic ring) is partially oxidized into a new molecule (depicted as an orange aromatic ring). Indirect photolysis occurs when the absorption of light leads to the production of reactive oxygen species (middle panel), such as singlet oxygen, peroxy radicals, and hydroxyl radicals. These reactive intermediates can oxidize a wide range of compounds, not just the compounds that directly absorb light (right panel).  $h\nu$  = light energy. (a) and (b) reproduced from Ward and Overton (2020) with permission

of oil by sunlight may influence oil trajectory at sea and the selection of response tools.”

In addition to potential implications for response strategies, photo-oxidation adds oil-soluble, oxidized chemicals to the oil mixtures. These oil-soluble oxy products, in essence, become a part of, for example, stranded oil residues, with properties similar to the oil’s resin and asphaltenic semi-solid/solid components stranded on beaches and marshes (see later section).

### **OIL-PARTICLE AGGREGATES, MARINE OIL SNOW, AND MARINE OIL SNOW SEDIMENTATION AND FLOCCULENT ACCUMULATION**

According to the Transportation Research Board and National Research Council (2003) review and recommendations, “Understanding the distribution of petroleum hydrocarbons between the dissolved phase and the variety of aquatic particles is important for determining the fate of hydrocarbons in the sea and the bioavailability of these chemicals to marine biota.”

The importance of the association of oil chemicals with mineral particles and with organic matter in sediments—called oil-particle aggregates or OPAs (formerly known as oil-mineral aggregates or OMAs; Burd et al., 2020; Passow and Overton, 2020)—was known as an important biogeochemical phenomenon for decades prior to the DWH spill (e.g., NRC, 1975, 1985). OPAs are particularly important in nearshore regions or in regions where land runoff or river discharges carry mud and silt particles into the ocean. This was described as a major phenomenon governing the fate of oil chemicals as early as the 1969 Santa Barbara spill (Kolpack, 1971).

It is also important to keep in mind that during the DWH accident there were attempts to shut down the well by pumping in drilling mud. The efforts failed, resulted in discharge of drilling mud mixed with DWH gas and oil chemicals near the sediment-water interface,

and likely led to the formation of OPAs, perhaps of a special type (Passow and Hetland, 2016, and references therein).

Marine snow has long been acknowledged as important in the ecology of marine environments (Silver, 2015). The involvement of the marine snow phenomenon in all biogeochemical cycles would likely be obvious to anyone with the privilege of viewing marine snow in situ. This was the case for author Farrington when he observed marine snow and easily resuspended floc in the deep ocean at the sediment-water interface out of a DSRV *Alvin* viewport during one 1976 dive and consequently changed his entire approach to a significant portion of his research effort (Farrington, 2020b).

Marine snow is defined as particles >0.5 mm in size and may consist of aggregations of smaller organic and inorganic particles, including bacteria, phytoplankton, microzooplankton, zooplankton fecal pellets and feeding structures (e.g., larval houses), biominerals, terrestrially derived lithogenic components, and detritus (Alldredge and Silver, 1988; Silver, 2015). Early in the research and assessments for the DWH oil spill, the issues of marine snow interacting with oil and becoming marine oil snow, or MOS, and then accumulating, flocculating, and sinking to the seafloor in the MOSSFA process were identified as important subjects for extensive research because of their apparent major roles in the biogeochemistry and fate of oil chemicals in the water column (Passow and Ziervogel, 2016; Daly et al., 2016). A GoMRI MOSSFA Working Group was formed in May of 2013 to facilitate interdisciplinary research and interactions among research groups and individuals conducting research connected with MOSSFA. The work of these scientists has culminated in several reviews summarizing MOSSFA-related results and the role of MOSSFA in the overall fate of the DWH oil chemicals (e.g., Burd et al., 2020; Daly et al., 2020; Kujawinski et al., 2020; Quigg et al., 2020; Passow and Overton, 2021).

Burd et al. (2020) pointed out three

earlier references that mention detritus of the marine snow type being present in oil spills. It seems clear that, prior to the DWH spill, with a few exceptions, studies focused mainly on interactions of mineral or sediment particles with oil chemicals in shallow-water environments (i.e., the *Tsesis* oil spill in 1977–1978; see Johansson et al., 1980, and references therein). These studies drew attention to the importance of biological detritus, particulate matter, and fecal pellets, such as those from zooplankton, in the water column biogeochemistry of petroleum hydrocarbons and deposition to sediments. In addition, mesocosm experiments using No. 2 fuel oil to mimic chronic oil inputs to shallower estuarine water columns recorded the accumulation of several millimeters of organic detritus-oil chemical accumulations at the sediment-water interface (Gearing et al., 1979).

The post-DWH lexicon regarding the fates and biogeochemistry of oil chemicals in the water column now includes consideration of MOS and MOSSFA in oil spill response, modeling, and research. An important finding of DWH research and assessments is the partitioning of chemicals between oil and particulate matter or the incorporation of oil chemicals in particulate matter such as marine snow that is followed by protracted deposition of oil-associated marine snow to the seafloor. During deposition, desorption/adsorption of the more soluble/less soluble oil chemicals continues along with microbial degradation of some of the oil chemicals. Reviews by Daly et al. (2016), Passow and Hetland (2016), Passow and Ziervogel (2016), Burd et al. (2020), Passow and Overton (2020), and Quigg et al. (2020 and 2021, in this issue)—and references therein—offer a comprehensive and up-to-date review of the state of knowledge about marine snow in oil spill situations and also offer suggestions for important next stages of research. These reviews also delve into important research findings from a combination of laboratory and mesocosm experiments, placed within the context of field observations,

concerning the interaction of oil hydrocarbons and Corexit dispersants with phytoplankton and bacteria. Of note are the interactions that stimulate phytoplankton and bacteria to exude extracellular organic matter such as biofilms or transparent exopolymeric particles, a subgroup of extracellular polymeric substances.

Burd et al. (2020) present and discuss evidence that MOS and MOSSFA were associated with the DWH oil spill. Their key points include:

**1. Visual observations** noted large, mucus-rich marine snow particles of about 10 cm in the surface water during May 2010. These marine snow particles seemed to contain oil and were observed near surface oil layers. They were not observed during a June cruise in the area.

**2. Sediment traps and camera systems** provided samples and observations documenting sedimentation events involving MOS in the water column during and after the spill (Diercks

et al., 2018). Interestingly, well before the DWH spill, Diercks and Asper (1997) had used a similar trap and camera system to measure settling velocities of aggregates and marine snow in the Gulf of Mexico's Mississippi River plume area. A Shadowed Image Particle Profiling Evaluation Recorder (Remsen et al., 2004) was also used to observe marine snow particles and MOS (Daly et al., 2020). We note that recovery of flocs from the tops of carefully collected cores and from slurp guns (e.g., Stout et al., 2016) also provided key samples of OMAs, MOS, and MOSSFA type events.

**3. Evidence from laboratory and mesocosm experiments** confirm field observations in general and provide greater insights into what most likely occurred in the field during and after the DWH spill.

a. Marine snow-sized bacterial oil aggregates (BOAs) that result from exopolymer production by bacteria were present. Passow and Overton

(2020) noted that photo-oxidation in surface waters may have enhanced the formation of BOAs.

b. Formation/sorption of exopolymer matrices on the surfaces of small oil droplets resulted in micro-BOAs.

c. Phytoplankton cells and detrital particles formed MOS aggregates with oil droplets in the aggregate matrix. These can sink rapidly.

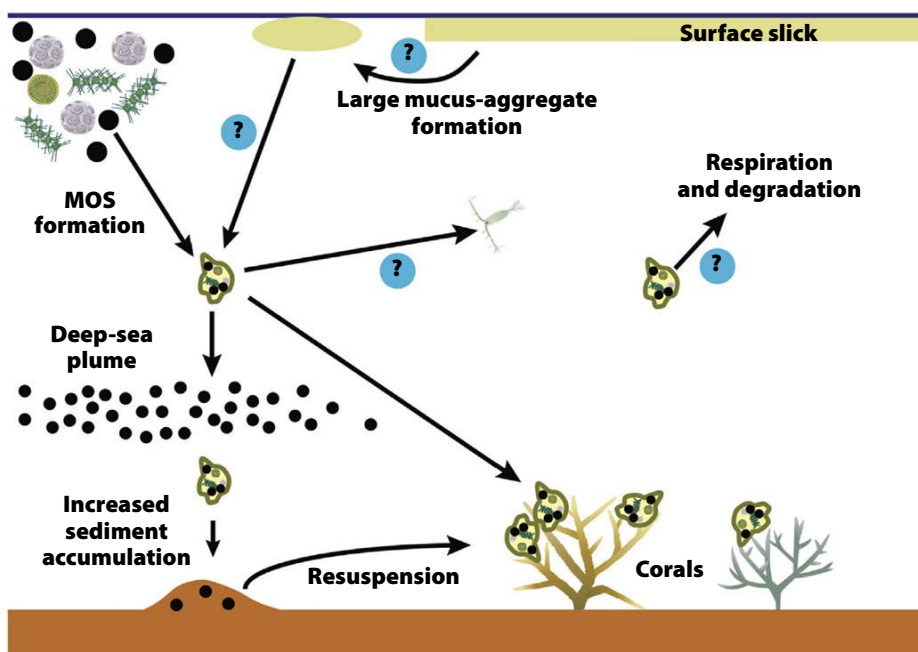
d. Although zooplankton contributions to MOS have not been as well studied (Almeda et al., 2016), it has been known for decades that zooplankton can ingest oil droplets or particles in the water column and then produce oil-containing fecal pellets that sink to the seafloor (e.g., Conover, 1971). This process was also observed in laboratory experiments with the zooplankton *Doliolidae* (*Doliolidae gegenaurai*) (R.F. Lee et al., 2012), and it is more than likely that this occurred during DWH.

Burd et al. (2020) provide an important observation: "Mesocosm experiments revealed that in the presence of oil and marine particles, aggregate formation was faster, and aggregates were colonized by higher densities of heterotrophic bacteria, than those formed in incubations without added oil (Quigg et al., 2016; Doyle et al., 2018)."

**4. Possible effects on deep-sea corals.**

The deposition of MOS on some deep-water corals via what was most likely a MOSSFA mechanism was noted in a few areas of the deep Gulf of Mexico (e.g., see Fisher et al., 2016). The MOS or floc material was sampled, analyzed, and shown with reasonable certainty to be composed of weathered DWH oil with some dioctyl-sodium sulfosuccinate (DOSS) from dispersant also present (see Fisher et al., 2016, and White et al., 2012, 2016, and references therein).

The Figure 5 schematic from Burd et al. (2020) summarizes the various MOS and MOSSFA processes discussed above.



**FIGURE 5.** A schematic of the processes involved in the formation of marine oil snow (MOS) and marine oil snow sedimentation and flocculent accumulation (MOSSFA) events, as well the impacts of MOS and MOSSFA on marine systems. Black dots depict oil droplets, the yellow rectangle shows the surface oil slick, and the yellow ellipse represents large mucus aggregates. Question marks indicate connections that scientists suspect occur, but for which few data have been collected. Reproduced from Figure 4 in Burd et al. (2020) with permission



The question marks indicate processes that these authors suspect occur but for which little data have been collected, and their paper discusses questions raised, including “what remains unknown?” We summarize by paraphrasing key points.

- What are the conditions during an oil spill that can lead to MOS and MOSSFA? Discharges from nearby rivers, individually or together, seem to be concomitant with suspended sediment, nutrient, and particulate organic carbon loads. Plankton blooms occur in the more open-ocean areas and appear to accompany or cause natural marine snow events.
- We need to know more about where in the water column marine snow becomes MOS as a result of the various mechanisms of sorption, scavenging, and incorporation of particles. During DWH, it appeared not only to be a surface water phenomenon but also to occur throughout the water column and especially in the subsurface plume(s).
- How is biodegradation of oil impacted by inclusion of oil into MOS?
- Interactions between oil chemicals and particles result in transforming the oil's composition.
- How can the densities and shapes of various MOS sizes be incorporated into models to provide computation of vertical and horizontal transport velocities?

## DEPOSITION AND LONG-TERM FATE IN OFFSHORE AND DEEP-SEA SEDIMENTS

Estimates of the amount of DWH weathered petroleum hydrocarbons deposited onto sediments of the northeast Gulf of Mexico, and of the area involved, vary depending on the sampling grid and the type of analysis, as summarized by Passow and Hetland (2016). They note that an estimated 2%–15% of the spilled oil was deposited after compositional change due to weathering, and that this could be considered a lower limit. Later estimates suggest  $21\% \pm 10\%$  (Romero et al., 2017).

The deposited material was weathered by dissolution and microbial degradation of oil residues originating from the subsurface plumes and by volatilization, photo-oxidation, and microbial degradation of oil that reached the sea surface.

There were several different assessments of DWH oil chemicals in surface sediments collected in deep water in the immediate region of the DWH well site during and after the spill, and also further afield in the northeast Gulf of Mexico. Sampling was largely supported by federal agencies via the NRDA process, by BP, and by GoMRI. Resulting data are all available online (<https://www.diver.orr.noaa.gov/deepwater-horizon-nrda-data/> and <https://data.gulfresearchinitiative.org/>; also see Zimmermann et al., 2021, in this issue). In addition to contributing to continuing studies of the DWH spill, we expect these data may be useful in the future, perhaps to test new hypotheses originating from laboratory or mesocosm studies, or to compare with results of future accidental oil inputs.

Sediment cores were collected with care to retain the floc (if present) at the sediment-water interface and within 8 km of the well site. Stout and Payne (2016a) report an important set of data from detailed chemical analyses of hydrocarbons in the upper 1 cm of sediment cores as well as of some deeper sections down to 10 cm; **Figure 6** provides the typical PAH composition of weathered oil residues they found in bottom surface sediments collected near the wellhead in 2011. Both the target alkanes (not shown here) and PAH compositions were significantly degraded in these oil residues, with some depleted by over 90%. Weathering of oil residues mainly occurred before deposition onto the seafloor and was mostly affected by dissolution and biodegradation in the submerged plumes and during vertical transport to the seafloor. Oil residues were least weathered near the well head and got progressively more weathered with distance from it, further suggesting that most weathering occurred before deposition on bottom

sediments. Deep time series sediment trap data are in accord with these results (Passow and Stout, 2020).

The data in **Figure 6** illustrate a significant aspect of the changing composition of the DWH aromatic hydrocarbons over time as the various biogeochemical processes influence their composition. Chrysene and alkyl chrysenes, and aromatic hydrocarbons of similar or greater molecular weight, become the dominant aromatic hydrocarbons in the oil residues even though they were not the dominant aromatic hydrocarbons in the original DWH oil spilled. This has implications for the assessment of aromatic hydrocarbons for long-term effects on organisms. Understandably, the past focus for testing short-term effects has been on the lower molecular weight aromatics, such as naphthalenes and phenanthrenes, that have been assayed and shown to have adverse effects, depending on the concentrations, types of exposure, and the organisms (e.g., NRC 1985; Transportation Research Board and National Research Council, 2003).

The vast majority of DWH oil residues in sediments were completely depleted of low and medium molecular weight hydrocarbons (e.g., carbon numbers below  $\sim n\text{-C}_{24}$ ) after three to four years (Bagby et al., 2016; Babcock-Adams et al., 2017). These represent oil residues with weathering losses of over 90% of their target hydrocarbon content when compared to the content of the Macondo oil when it was spilled into the Gulf. However, it should be noted that, in addition to mineralization and  $\text{CO}_2$  production, some of the hydrocarbon compounds lost during weathering were converted into oil-soluble oxidized compounds (White et al., 2016; Aeppli et al., 2018), which are generally not detected by target compound GC-MS analyses. Thus, the 90% loss does not mean that 90% of the original oil compounds were fully oxidized to  $\text{CO}_2$  (i.e., removed).

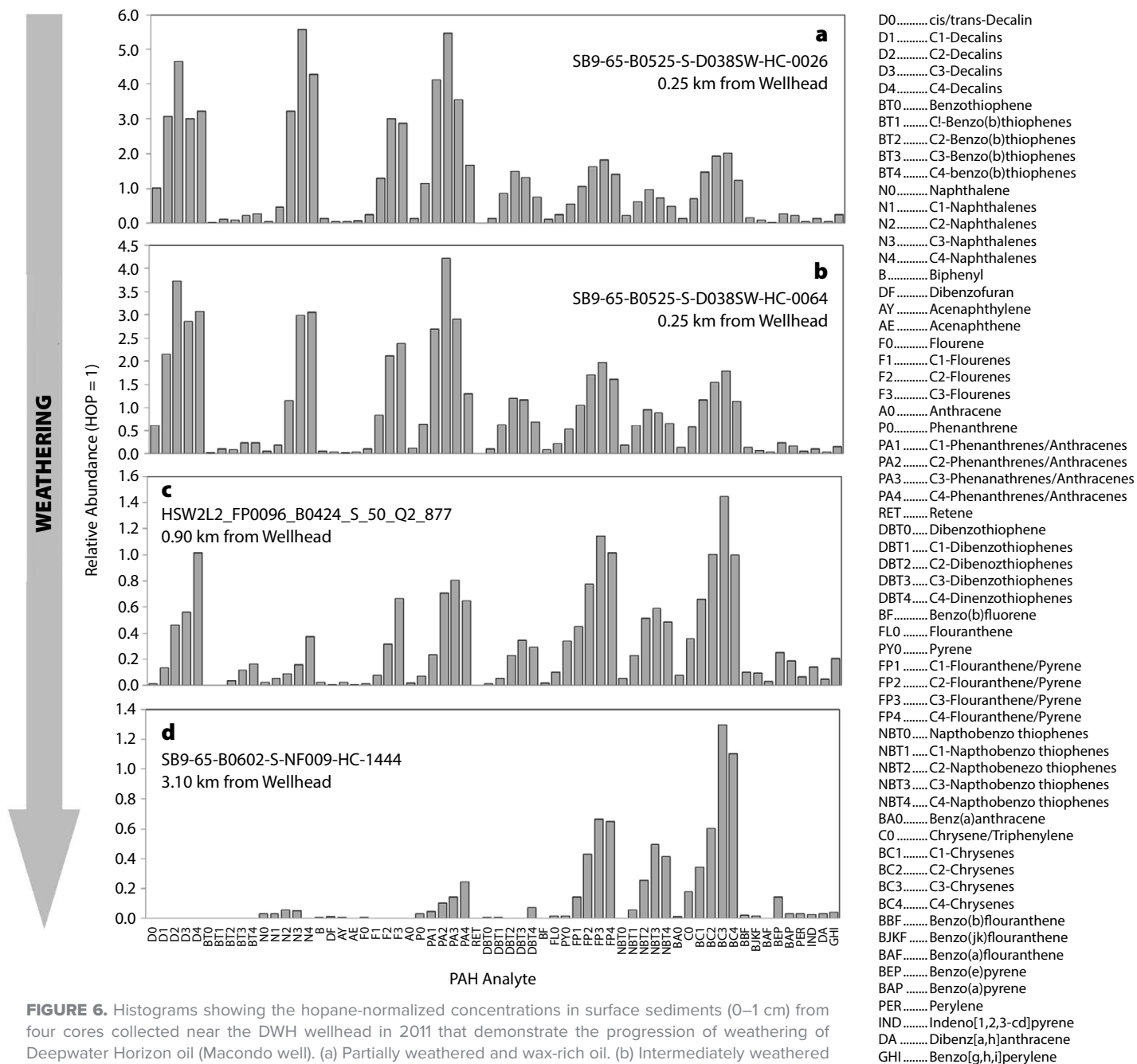
To frame sampling, measurements, and estimates of DWH oil deposition, Brooks et al. (2015) provide the various sedi-

ment types known in the northern Gulf of Mexico region for the continental shelf, slope, and canyons. These authors and Romero et al. (2015) document a depositional pulse extending about 100 nautical miles (~185 km) from the DWH site to the northeast in the DeSoto Canyon area for water depths ranging from about 300 m to 1,500 m. Romero et al. (2017) depict oil

and MOS deposition extending 270 nautical miles (500 km) to the southwest of the spill site with an area of 110,000 km<sup>2</sup>. After the leak was closed, Yan et al. (2016) deployed a deep time-series sediment trap in that area above the sediment-water interface at 1,538 m water depth between August 2010 and October 2011. They reported deposition of DWH spill-

related oil chemicals, drilling mud chemicals (presumably from the failed attempt to shut the well with drilling mud), and black carbon particles from the in situ burning of the oil slick, which was one of the response mechanisms (Rullkötter and Farrington, 2021, in this issue).

Daly et al. (2016) provide a detailed and informative review of the vari-



**FIGURE 6.** Histograms showing the hopane-normalized concentrations in surface sediments (0–1 cm) from four cores collected near the DWH wellhead in 2011 that demonstrate the progression of weathering of Deepwater Horizon oil (Macondo well). (a) Partially weathered and wax-rich oil. (b) Intermediately weathered and wax-rich oil. (c) Highly weathered and wax-rich oil. (d) Severely weathered and wax-rich oil. Wax-rich oil contains a high concentration of *n*-alkanes, also called normal paraffins. The x-axis shorthand notations for aromatic hydrocarbons analyzed are listed at right with full compound names written out in the order they are shown left to right on the x-axis. Figure and compound names and abbreviations (with some modifications) reproduced from Stout and Payne (2016a) with permission

ous origins of sinking OPAs, MOS, and MOSSFA, and factors that might or did control their deposition to the seafloor. Sediment cores provided a multi-proxy record of MOSSFA events, the intensity of the flux of oil chemicals to the seafloor, and the spatial extent of such deposition and post-depositional events.

Bagby et al. (2016) examined 125 aliphatic (saturated hydrocarbons), aromatic, and biomarker compounds (Rullkötter and Farrington, 2021, in this issue) in 2,908 sediment samples collected within four years of the spill. The data they interrogated are available from the NRDA website and in the supplementary materials for Bagby et al. (2016). They demonstrate the importance of chemical structure, physical chemical form (e.g., large and small OMA and MOS particles), and hydrocarbon persistence for sample locations containing higher initial concentrations at the time of deposition.

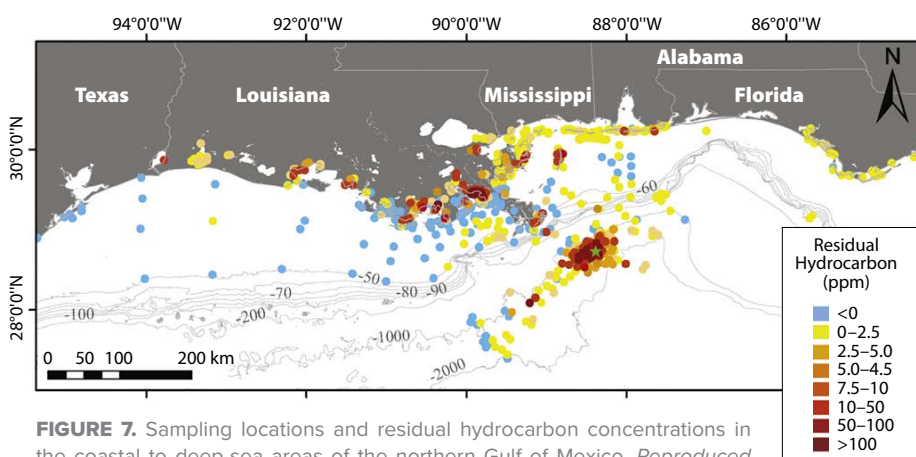
Romero et al. (2017) combined their own samples with a large, archived data set in order to interpret 158 hydrocarbon compounds in 2,613 sediment cores, several of which overlapped the data set accessed by Bagby et al. (2016). Romero et al. (2017) assessed the chemical signature of DWH oil in surface sediments to determine the amount, distribution, and areal extent of DWH oil residues deposited on the seafloor from coastal, continental shelf, and deep-sea areas of the northern Gulf of Mexico. The total residual hydrocarbon concentrations deposited at each site based on the 2010–2011 sampling that they found is depicted on the spatial chart in Figure 7 and grouped in coastal, continental shelf, and deep-sea stations in Figure 8. Their work revealed relatively large deposition of weathered oil chemicals in the coastal and deep-sea areas and very little deposition on the continental shelf. Large spatial heterogeneity of deposits is a consequence of spatial variability in sedimentation rates, resuspension of deposited material, and lateral transport.

Giering et al. (2018) measured sedimentation rates of polycyclic aromatic

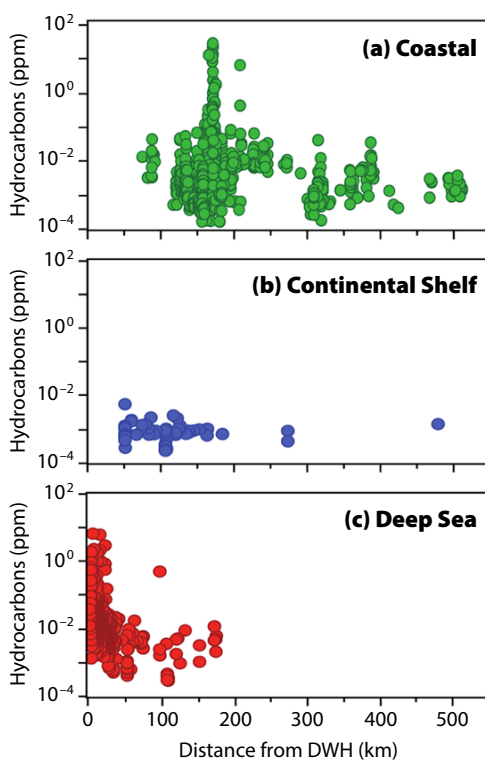
hydrocarbons with time-series sediment traps at three contrasting sites in the northern Gulf of Mexico: a station near the DWH site (1,660 m water depth), a natural seep site (1,380 m water depth), and a reference site (1,160 m water depth). They summarized sedimentation rates of organic carbon and other proxies for marine particles as well as hydrocarbon compounds for the period 2012 to 2016. They concluded that the quality and quantity of sedimentation at each site were very different and ascribed this to differences in relative riverine and oceanic influences

as well as inputs from natural seepage and combustion product PAHs—the latter most likely from land sources via atmospheric transport and/or runoff. Modeling efforts comparing two of the traps provide clear documentation and mechanistic explanations of the complex variability of vertical fluxes due to “mesoscale circulation and seasonal cycle of primary production, which in turn are linked to riverine inputs, wind forcing and the seasonal cycle of the mixed layer” (Liu et al., 2018).

Diercks et al. (2018) discuss observations and accompanying interpretations



**FIGURE 7.** Sampling locations and residual hydrocarbon concentrations in the coastal to deep-sea areas of the northern Gulf of Mexico. *Reproduced from Romero et al. (2017) with permission*



**FIGURE 8.** Spatial extent of contaminated sediments found in the northern Gulf of Mexico after the Deepwater Horizon spill. Data are shown for (a) coastal, (b) continental shelf, and (c) deep-sea areas. Contaminated sediments contain higher  $\Sigma$ Hydrocarbons in the surface layer (post-spill) compared to down-core layers (background, pre-spill) of the sediment cores analyzed. The cores were collected in 2010–2011.  $\Sigma$ Hydrocarbons refer to the sum of aliphatics (*n*-alkanes  $C_{10-40}$ , isoprenoids, branched alkanes), polycyclic aromatic hydrocarbons (2–6 ring, including alkyl homologues), hopanoids ( $C_{27-25}$ ), steranes  $C_{27-29}$ , and tri-aromatic steroid compounds ( $C_{26-28}$ ). *Reproduced from Romero et al. (2017) with permission; details of sampling locations are therein*



of resuspension of deposited MOS using a rich set of data from moored flux cameras, a profiling camera, current meters, and sediment trap sampling from fall 2012 to summer 2013, including the period of Hurricane Isaac. They concluded that while hurricane resuspension events are large scale, they become part of the averaged long-term background signal. Their observations and interpretations led them to suggest that small-scale resuspension events play an important role in redistributing sediment on the seafloor. This did not include the separate and rarer issue of hurricane-induced turbidity flows of unstable slope sediments as noted for the Taylor Energy Platform briefly discussed earlier (Bryant et al., 2020).

Physical oceanography observations and models (Boufadel et al., 2021, in this issue) indicate it is likely that DWH oil chemicals in the deep plume were transported horizontally by currents until they contacted sediments on the continental slope, where they were deposited and incorporated into surface sediments or were subject to resuspension and redeposition events elsewhere on the slope.

The potential deposition of oil residues remaining after in situ burning, which was used as a response measure to reduce oil mass in the slicks (see Rullkötter and Farrington, 2021, in this issue), is not well described, although Stout and Payne (2016b) did explore how much of the burn residue was deposited to the seafloor. They sampled a few burn residues from the sediment-water interface and provided a rough estimate that between 26,800 kg and 37,800 kg of PAHs (they measured concentrations of 51 PAHS) were deposited with the burn residues. They also stressed that the in situ burn process had reduced by 89% the mass loadings of PAHs that otherwise would have been contributed to Gulf of Mexico ecosystems.

The immediate and longer-term fate of the synthetic-based drilling mud (SBM) used in attempts to stop the DWH accident's oil and gas release and its input to surface sediments near the wellhead was

examined by Stout and Payne (2017). They tracked the distribution of SBM-derived  $C_{14}$ – $C_{20}$  olefins in space and time. In summary, they found these compounds, mixed with DWH oil chemicals, in surface sediments as deep as 10 cm and extending for 6.5 km<sup>2</sup> around the well site. They noted a decrease in concentrations of the olefins in most of the sediments by a factor of 10 between 2010/2011 and 2014, most likely due to biodegradation. Based on their own and other data, they projected that weathered SBM olefins released during the DWH disaster would likely persist in detectable concentrations in the deep-sea sediments of all or parts of this area for up to 13 years.

### **FATE ON SHORELINES: BEACHES AND MARSHES**

Standardized surveys were instituted early in the spill to assess where DWH oil came ashore along the coastal areas of the northern Gulf of Mexico. Michel et al. (2013) reported 1,773 km of the 7,058 km of beaches and coastal marshes from Florida to Texas received DWH oil at various stages of weathering. Louisiana accounted for 60.6% of the oiled shoreline, and 38% of that shoreline remained visually oiled after two years. Past experience suggested that there were no effective methods for cleaning oil from marshes; those tried had resulted in large adverse effects to the marshes (NRC, 1985). However, cleaning of oil deposited on beaches had developed into an acceptable practice, and extensive efforts were made to remove the visible oil from beaches fouled by the weathered oil.

#### **Beaches**

A total of 925 km of beaches were polluted by DWH oil (Huettel et al., 2018, and references therein). Most of the oil came ashore as a floating water-in-oil emulsion, for example, as “mousse.” It was known from research conducted after other oil spills that heavily weathered oil residues buried in beaches could persist for years to decades (Huettel et al., 2018, and references therein). Thus, there

was a relatively rapid and significant response effort to remove the clearly visible oil from affected beaches.

Despite these efforts, normal movement of sand due to wind, waves, and human activities resulted in burial of oil sheets and sand-oil aggregates (SOAs) of various sizes. The initial cleanup response was followed by Operation Deep Clean, which involved digging and sifting for SOAs, and the resulting removal of most of the large ones (Huettel et al., 2018, and references therein). Despite these efforts, small SOAs or surface residual balls (SRBs), depending on the authors' designations, remained hidden in the beach sand. In some locations there were “tar patties” on the sand and buried layers of SOAs and submerged oil mats (SOMs) nearshore. Storm waves mixed the remaining SOAs and tar patties into the beaches or resurfaced and even resuspended them, leading to the reappearance of oily sand on cleaned beaches (Hayworth et al., 2015; John et al., 2016). This was still happening at a reduced rate as of September 2017 (Huettel et al., 2018; Bociu et al., 2019).

Because a variety of approaches was used for field sampling along the coast, comparisons were challenging and required that syntheses of data and interpretations take temporal and spatial variations into account. Nevertheless, field studies that included sampling and analyses of SOAs and tar patties for oil chemicals and reaction products along with microbial ecology/omics have yielded substantive new knowledge about fates of oil residues on/in beaches (John et al., 2016; White et al., 2016; Bostic et al., 2018; Huettel et al., 2018; Bociu et al., 2019). In addition, experiments explored the effects of light exposure (John et al., 2016) or the weathering of aging buried SOAs over several years (Bociu et al., 2019). The latter experiments suggested that SOAs buried deep in beach sand can be decomposed relatively rapidly by aerobic microbial degradation. The key enabler is the tidally ventilated permeable beach sand. Despite this process, given the high molecular weight constituents in

the residual oil and the addition of photo-chemically or microbially generated oxygenated reaction products, Bociu et al. (2019) estimated that complete decomposition of SOAs buried in sand may take as long as three decades. Besides removal by mechanical means, microbial degradation, photo-oxidation (most likely mainly before stranding), and the loss by water washing/dissolution governed the fate of oil chemicals as well as microbial degradation and photo-oxidation reaction products within SOAs and tar patties.

It is important to consider the findings of Aeppli et al. (2018), who discuss emulsions/slicks that come ashore containing substantially weathered oil or oil that has been subjected to photo-oxidation. Between 2011 and 2017, the alkane and aromatic hydrocarbon fractions of the oil residues in the sand patties were depleted by  $79 \pm 2\%$  compared to original DWH oil. The analyses done by Aeppli et al. (2018) document that the loss of alkanes and aromatics was partly compensated by a simultaneous increase in the production of the oil soluble OxHC fraction. Thus, the overall decrease of oil-derived chemicals in sand patties was only  $\sim 42\% \pm 12\%$  between 2011 and 2017 when compared to the composition of original DWH oil. Further experiments demonstrated that the water-soluble fraction of the OxHCs was relatively small, for example, on the order of 0.1% to 1%, indicating that the OxHCs retained significant hydrophobicity, thereby promoting sorption or association with the resin-like or asphaltene-like residues in the sand patties. Bostic et al. (2018) demonstrated that microbes were utilizing either residues from DWH spilled oil or the OxCHs as a source of carbon by measuring the depletion of  $^{14}\text{C}$  in phospholipid fatty acids.

Challenges for the future include establishing the exact reaction pathways for both microbial and photochemical reactions, the products of these reactions, and the potential for environmental effects of these reaction products. A potential human health concern is the ingestion by toddlers on beaches of very small SOAs

(and their associated chemicals) missed by beach cleaning response efforts or generated from nearshore sand-oil mixtures brought ashore after the beach cleaning response (Sandifer et al., 2021, in this issue, and references therein).

### Marshes

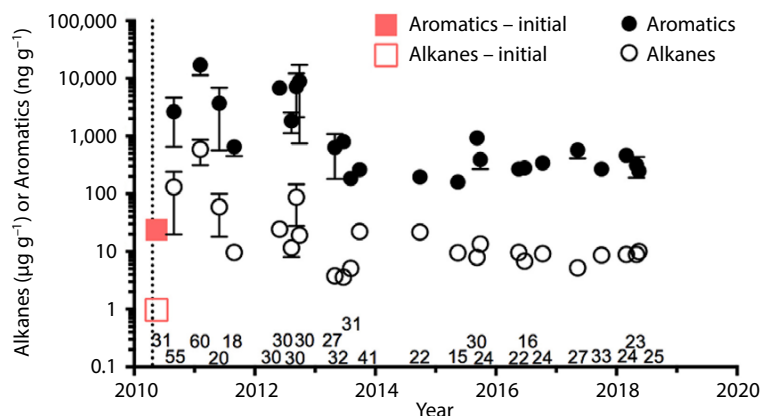
The DWH spill extensively oiled portions of northern Barataria Bay, Louisiana, marshes. Atlas et al. (2015) analyzed samples from 20 marsh sites for the years 2011, 2012, and 2013 and documented both spatial and temporal variability in the presence of DWH oil and the response of the microbial community to its residues. The 2011 marsh samples exhibited significant oil losses due to weathering and biodegradation, which may have occurred in transit to the marsh site or shortly thereafter. The lower molecular weight alkanes (below  $n\text{-C}_{15}$ ) and aromatic hydrocarbons (below the three-ring phenanthrene/anthracene and their alkylated homologues) that were present in the discharged oil were not present or were detectable only in trace amounts in samples from the marshes. The chemical compositions of the hydrocarbons indicate that both weathering (volatilization and dissolution) and microbial biodegradation are responsible for the losses. This work by Atlas et al. (2015) is one of the few studies to date of the fate of DWH oil in marshes that examines microbial community composition and species abundance in parallel with analyses for alkanes and aromatic hydrocarbons. Examples of other such studies are Engel et al. (2017) and Tatariw et al. (2018). See Weiman et al. (2021), in this issue, for a discussion of microbial genomics and related matters.

Atlas et al. (2015) further reported that between 2011 and 2013, loss of oil chemicals proceeded in the upper 0–2 cm of their sampling sites. Biodegradation and/or dissolution to pore waters or overlying waters due to tidal and storm flushing led to significant decreases in concentrations of the higher molecular weight  $\text{C}_{15}$  to  $\text{C}_{40}$  alkanes and of higher molecular weight phenanthrene to alkylated

chrysene aromatic hydrocarbons. Similar results of patchiness and weathering/biodegradation of DWH oil in transit or shortly after arrival in the marsh were reported for five sites in the subtidal and intertidal area of Barataria Bay sampled 18 months after the spill (Kirman et al., 2016). Using oil chemical signature or “fingerprinting” techniques, Meyer et al. (2018) observed redistribution of oil buried below the upper 0.5 cm in Bay Baptiste, Louisiana, marsh after Hurricane Isaac.

Over eight years, Turner et al. (2019) pursued a more comprehensive study of the fate of oil and oil residues in marsh sediments of Barataria Bay as part of the multi-year Coastal Waters Consortium effort funded by GoMRI (see Figure 3 for sampling locations). The concentrations of 28 individual alkanes and 43 polycyclic aromatic hydrocarbons and their respective alkyl homologues (i.e., 18 parent PAHs and 25 alkyl homologue groups) were analyzed. Initially, the higher concentrations of oil alkanes and aromatics were found in the samples nearest to marsh edges (i.e., 1 m into the marsh from the shoreline compared to 10 m from the shoreline), and the oiling was uneven overall. As time progressed, the uneven nature of oiling was replaced by more uniform distribution of oil residues in the marsh sediments, presumably by tidal and stormwater actions.

The total concentrations of alkanes and the aromatic hydrocarbons as a function of time over the period 2010 to 2018 are plotted in Figure 9. There are significant decreases in concentration over the first few years, in the range of 70% to 90% losses, depending on the specific compound. Thereafter, loss rates decreased, and concentrations leveled. In 2018, concentrations were at least an order of magnitude higher than initial concentrations, when there were no DWH oil residues. These elevated concentrations are of concern in the longer term, for example, with respect to their effects on marsh grass roots and subsequent erosion and their effects on the behaviors of marsh animals (e.g., fiddler crabs), as discussed by Turner



**FIGURE 9.** The concentrations of total aromatics (filled symbols,  $\text{ng g}^{-1} \pm \text{SE}$ ) and total alkanes (open symbols  $\mu\text{g g}^{-1} \pm \text{SE}$ ) in marsh sediments for each sampling trip from May 2010 to May 2018. The red symbols indicate samples taken before oil reached the marshes. The vertical dotted line is the beginning of the Deepwater Horizon oil spill offshore. The average number of samples taken for individual trips appear below each sampling symbol (along the x-axis) and are the same for alkanes and aromatics. Reproduced from Turner et al. (2019) with permission

et al. (2019, and references therein).

We know that the higher molecular weight resins and asphaltenes were part of the water-in-oil emulsions that came ashore (see earlier discussions this paper). Chen et al. (2016) conducted detailed analyses of extracts from Barataria Bay marsh surface sediments using FT-ICR-MS, a powerful analytical chemistry method (Rullkötter and Farrington, 2021, in this issue, and references therein for a description). They reported the presence of some of the higher molecular weight compounds found in DWH resins and asphaltenes. These are among the first, if not the first, of these types of measurements for oil-contaminated marshes. They documented incorporation of carboxylic acid into the parent DWH hydrocarbons. Furthermore, there was a significant increase, over 48 months, in high molecular weight oxygenated compounds containing four to six oxygens, compounds not found in the resins and asphaltenes of the DWH oil. The combined results of these analyses, which used two-dimensional gas chromatography with both a flame ionization detector and a mass spectrometer detector, and ultra-high-resolution FT-ICR-MS indicate that both biodegradation and photo-oxidation caused molecular mod-

ification of the oil residues in the marsh. There was accumulation of some higher molecular weight oxy-generated products in the resin and asphaltene extracts of the marsh sediments. The asphaltenic-like material in shoreline mats hampers vegetative regeneration of marsh shorelines for at least several years (Lin et al., 2016). Furthermore, observations note that less weathered oil resides in fiddler crab burrows and in packets under vegetated tar mats, suggesting the existence of conditions that retard degradation of oil residues.

### BIOAVAILABILITY OF OIL CHEMICALS IN THE GULF ECOSYSTEMS

The term *bioavailability* refers to a chemical being in a physical or chemical form (e.g., sorbed to particles, incorporated into marine oil snow, or dissolved) that can be either ingested by marine organisms or taken up across cellular or membrane surfaces (e.g., marine animal gills). Prior to the DWH accident and spill, there was a growing understanding of the general processes and factors governing the bioavailability, uptake, metabolism, excretion, and food web transfer in marine organisms for specific constituents of oil in the molecular weight range

between  $n\text{-C}_{14}$  and  $n\text{-C}_{35}$  alkanes and branched alkanes, and polynuclear aromatic hydrocarbons in the range of naphthalenes to dibenzophenanthrenes. Most of this knowledge was gained from a combination of field observations, modeling exercises, and laboratory and mesocosm experiments in estuarine, coastal, and continental shelf ecosystems (e.g., NRC, 1985; Transportation Research Board and National Research Council, 2003; Mitchelmore et al., 2020).

During DWH, there was a significant effort to assess the safety of seafood that might be contaminated to the extent that it was unsafe for human consumption. More than 8,000 samples of common seafood fish and bivalves were analyzed for a specified group of aromatic hydrocarbons (Ylitalo et al., 2012; reviewed in Dickey and Huettel, 2016). Understandably, because of the urgency of protecting public health while not adversely impacting the fishing economy, the study focus was on PAHs. Unfortunately, this meant that analyses of other DWH hydrocarbons were not done. Such a broader analysis might have provided an assessment of oil biomarker compounds over a wide geographic area, which could have provided more clues about oil uptake by these organisms.

Mitra et al. (2012) report measurements of several PAHs in mesozooplankton sampled in August and September 2010 in the northern Gulf of Mexico. The data indicate contamination of the zooplankton by petroleum PAHs and are consistent with contamination by DWH oil residues. Oil droplets were also present in fecal pellets of zooplankton (Almeda et al., 2016).

Murawski et al. (2014) and Snyder et al. (2015) conducted an extensive study of offshore demersal fishes in 2011–2013 with assays for naphthalene and benzo(a)pyrene metabolites. There was evidence of an episodic increase and then decrease for naphthalene metabolites in red snapper and kingsnake eel. Golden tilefish exhibited the highest concentrations of naphthalene metabolites, concentra-



tions that persisted for the study period. The benzo(a)pyrene metabolites were the same for all species and were low when compared to data from studies reported in the literature for other spills.

A pioneering study by Romero et al. (2020) measured PAHs in deep-sea cephalopods in the northern Gulf of Mexico. They analyzed samples from 2001 (pre-spill), 2010, and 2015–2016, and reported episodic exposure to petrogenic hydrocarbons in 2011 and continuing through 2015–2016. This is consistent with the presence of DWH oil in these waters and on particulate matter, as reported above.

It was beyond the scope of our review to consider all of the Natural Resource Damage Assessment studies and reports relative to organism contamination by DWH oil chemicals. However, we direct readers' attention to an important study of deep-sea benthic red crabs (*Chaceon quinque-dens*) that were sampled at several stations near the DWH site, at oil seeps, and at historic sites by Douglas et al. (2018).

Isotopic signatures of carbon,  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ , in petroleum can be used as rough tracers of DWH chemicals, as they were taken up, biodegraded, and metabolized as they passed through Gulf of Mexico ecosystem food webs. As with other chemical analyses, a consideration is that there may be other petrochemical sources contributing to the samples being analyzed. That said, Graham et al. (2010), Chanton et al. (2012), Quintana-Rizzo et al. (2015), and Wilson et al. (2016) collectively traced isotopic signatures consistent with DWH oil residues in some of the planktonic, coastal, and mesopelagic food webs.

In summary, field measurements reporting concentrations of PAHs or PAH metabolites in several species in the northern Gulf of Mexico are consistent with the presence of DWH oil residues in the region's water, particulate matter, and surface sediments. Isotopic signatures of  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ , also consistent with DWH oil residues, have been detected within some northern Gulf of Mexico ecosystems. Future studies might also consider research that assesses the efficacy

of measuring biomarkers.

The bioavailability of the higher molecular weight components of crude oils (e.g., resins and asphaltenes) and reaction products of photo-oxidation and microbial degradation, as well as combinations of the two processes, have yet to be the subject of concerted research efforts.

## SUMMARY

A wealth of new information on the fate of oil injected into the ocean from a well blowout at 1,500 m water depth was gained with funding from the Gulf of Mexico Research Initiative, the Natural Resource Damage Assessment for the Deepwater Horizon spill, BP, and government agencies, including the US National Science Foundation. This research has documented that photo-oxidation was a significant process acting on the surface oil slick very early in the spill, and that it played a significant role in the fate of the spilled oil. Photo-oxidation had been downplayed for decades despite earlier research in the 1970s and 1980s suggesting that it would be an important research topic.

Although marine snow and the process of sorption of oil chemicals onto particulate matter have long been recognized as important in marine biogeochemical cycles, the term marine snow was not mentioned in oil spill fate and effects literature in any meaningful manner until the DWH oil spill, when it became a topic of interest almost immediately as a result of field observations. The term marine oil snow and marine oil snow sedimentation and flocculent accumulation have now become prominent in the oil spill fate and effects scientific literature. MOS and MOSSFA are recognized as important components of the fate and effects processes post spill and especially in delivering oil residues to seafloor sediments and into the food webs of water column ecosystems.

Deposition, resuspension, and redeposition moved sediment contaminated with weathered and biodegraded DWH oil among benthic ecosystems. Little, if any,

long-term accumulation took place on the continental shelf due to resuspension and transport to the continental slope, where several areas were contaminated by MOS deposition from overlying waters, deposition of resuspended and horizontal/vertical transported material, or impingement of the subsurface plume in a few cases. Contamination of continental slope surface sediments was uneven but measurable in several places, and detectable oil residues lasted in some deep sediment areas for at least three years.

Despite extensive cleaning of oil from beaches as part of oil spill response activities, small amounts of residual oil remained on beaches as sand oil aggregates, surface-residual balls, and small tar patties. Combinations of photo-oxidation and microbial degradation proceeded, depending on environmental conditions (e.g., exposure to light, availability of oxygen). Analyses of the higher molecular weight resins, resin-like material and asphaltenes, and asphaltene-like material indicated small residues containing microbial degradation and photo-oxidation products continue to be present in beach sands and will most likely last for years to decades.

Studies of the oiled marshes in Barataria Bay, Louisiana, documented that initial oiling at the edges of marshes would soon be spread by tides and storms. Due to this dilution and to weathering, concentrations of oil residues decreased markedly for the first few years until they were about a factor of 10 more than background and were still at that level when last sampled in 2018. Analyses of a few samples using advanced analytical chemistry methods (FT-ICR-MS) documented the presence of higher molecular weight, resin-like and asphaltene-like material being added over time by a combination of photo-oxidation and microbial degradation. Less weathered DWH oil residues exist under vegetative mats and in fiddler crab burrows in impacted marsh environments.

Lastly, the development of relatively easily accessible and extensive data archives have proven to be helpful

for follow-on research by the scientific community at large. We believe that this will continue to be the case for years into the future.


## CHALLENGES FOR THE FUTURE

Here are a few important challenges that have arisen from DWH research:

- Successfully incorporating the knowledge gained regarding photo-oxidation, MOS, and MOSSFA into models of the fates and effects of spilled oil, including response models. There are indications that this has begun already (e.g., Ward et al., 2018, and as noted by Westerholm et al., 2021, in this issue).
- Understanding and documenting the influence of mitigation measures/techniques, such as aerial dispersant applications and in situ burning, on the movement of weathered oil into MOS and into the water column and to deep sediments by MOSSFA events (Quigg et al., 2021, in this issue).
- More extensively applying the advances in analytical chemistry to samples from various components of the ecosystem to better document reaction pathways for the fates of various oil chemicals.
- Continuing to advance understanding of the important photo-oxidation

reaction pathways and rates for oil on the sea surface and oil residues on beaches and in marshes.

- Simultaneously applying advanced analytical chemistry techniques and advanced genomic/proteomic analyses to samples from field observations and laboratory and mesocosm experiments in order to maximize rich data sets that will lead to new discoveries with respect to the fates of oil inputs (e.g., biodegradation) and responses of specific biological processes to specific oil chemicals.
- Understanding the long-term weathering, persistence, impacts, and fates of high molecular weight resin and asphaltenic and oxyhydrocarbon residues in deep-sea, coastal, beach, and marsh environments.
- Developing useful and accurate ways to budget the fate of spilled oil over time. We recognize that initial responses to oil spills need early estimates of fates of spilled oil. However, as time progresses in specific oil spill situations, there is a need to recognize that oil budgets are inherently compromised as each specific oil compound has its own fate, theoretically requiring its own budget. Bulk oil budget estimates not based on

compound-specific analysis are thus problematic. Moreover, any one compound may have successively different fates: for example, compounds that are dissolved or dispersed likely later biodegrade, but should not be categorized into both fates within the same budget. Due to the dynamic nature of spilled oil, any budget can only reflect a specific point in time. Combining estimates of processes measured in different units or spanning different timescales will generate budgets of questionable relevancy. 

## REFERENCES

- Aeppli, C., R. Swarthout, C.W. O'Neil, S.D. Katz, D. Nabi, C.P. Ward, R.K. Nelson, C.W. Sharpless, and C.M. Reddy. 2018. How persistent and bioavailable are oxygenated Deepwater Horizon oil transformation products. *Environmental Science & Technology* 52:7,250–7,258, <https://doi.org/10.1021/acs.est.8b01001>.
- Allredge, A.L., and M.W. Silver 1988. Characteristics, dynamics, and significance of marine snow. *Progress in Oceanography* 20(1):41–82, [https://doi.org/10.1016/0079-6611\(88\)90053-5](https://doi.org/10.1016/0079-6611(88)90053-5).
- Almeda, R., T.L. Connelly, and E.J. Buskey. 2016. How much crude oil can zooplankton ingest? Estimating the quantity of dispersed crude oil defecated by planktonic copepods. *Environmental Pollution* 208:645–654, <https://doi.org/10.1016/j.envpol.2015.10.041>.
- Atlas, R.M., D.M. Stoekel, S.A. Faith, A. Minard-Smith, J.R. Thorn, and M.J. Benoit. 2015. Oil biodegradation and oil-degrading microbial populations in marsh sediments impacted by oil from the Deepwater Horizon well blowout. *Environmental Science & Technology* 49:8,356–8,366, <https://doi.org/10.1021/acs.est.5b00413>.
- Babcock-Adams, L., J.P. Chanton, S.B. Joye, and P.M. Medeiros. 2017. Hydrocarbon composition and concentration in the Gulf of Mexico sediments in the 3 years following the Macondo well blowout. *Environmental Pollution* 229:329–338, <https://doi.org/10.1016/j.envpol.2017.05.078>.
- Bagby, S.C., C.M. Reddy, C. Aeppli, G.B. Fisher, and D.L. Valentine. 2016. Persistence and biodegradation of oil at the ocean floor following Deepwater Horizon. *Proceedings of the National Academy of Sciences of the United States of America* 114(1):E9–E18, <https://doi.org/10.1073/pnas.1610110114>.
- Bianchi, T.S., and E.A. Canuel. 2011. *Chemical Biomarkers in Aquatic Ecosystems*. Princeton University Press, Princeton, NJ, 396 pp.
- Bociu, I., B. Shin, W.B. Wells, J.E. Kostka, K.T. Konstantinidis, and M. Huettel. 2019. Decomposition of sediment-oil-agglomerates in a Gulf of Mexico sandy beach. *Scientific Reports* 9:10071, <https://doi.org/10.1038/s41598-019-46301-w>.
- Boehm, P.D., K.J. Murray, and L.L. Cook. 2016. Distribution and attenuation of polycyclic aromatic hydrocarbons in Gulf of Mexico seawater from the Deepwater Horizon oil accident. *Environmental Science & Technology* 50:584–592, <https://doi.org/10.1021/acs.est.5b03616>.
- Boehm, P.D., J. Pietari, L.L. Cook, and T. Saba. 2018. Improving the rigor of polycyclic aromatic hydrocarbon source fingerprinting. *Environmental Forensics* 19(3):172–184, <https://doi.org/10.1080/15275922.2018.1474287>.

**DEDICATION.** To David Hollander (1959–2020) of the University of South Florida, whose enthusiasm for research was infectious and who made numerous important contributions to oil spill research. David is shown aboard R/V *Justo Sierra* during sampling in 2015 near the site of the 1979 Ixtoc 1 oil well blowout in the southern Gulf of Mexico.



- Boesch, D., and N. Rabalais. 1987. *Long-Term Environmental Effects of Offshore Oil and Gas Development*. Elsevier Applied Science, New York, 708 pp., <https://doi.org/10.4324/9780203497777>.
- Boufadel, M., A. Bracco, E.P. Chassignet, S.S. Chen, E. D'Asaro, W.K. Dewar, O. Garcia-Pineda, D. Justić, J. Katz, V.H. Kourafalou, and others. 2021. Physical transport processes that affect the distribution of oil in the Gulf of Mexico: Observations and modeling. *Oceanography* 34(1):58–75, <https://doi.org/10.5670/oceanog.2021.117>.
- Bostic, J.T., C. Aeppli, R.F. Swarthout, C.M. Reddy, and L. Ziolkowski. 2018. Ongoing biodegradation of Deepwater Horizon oil in beach sands: Insights from tracing petroleum carbon in microbial biomass. *Marine Pollution Bulletin* 126:130–136, <https://doi.org/10.1016/j.marpolbul.2017.10.058>.
- Brooks, G.R., R.A. Larson, P.T. Schwing, I. Romero, C. Moore, G.-J. Reichart, T. Jilbert, J.P. Chanton, D.W. Hastings, W.A. Overholt, and others. 2015. Sedimentation pulse in the NE Gulf of Mexico following the 2010 DWH Blowout. *PLoS ONE* 10(7):e0132341, <https://doi.org/10.1371/journal.pone.0132341>.
- Bryant, W.L., R. Camilli, G. Burch Fisher, E.B. Overton, C.M. Reddy, D. Reible, R.F. Swarthout, and D.L. Valentine. 2020. Harnessing a decade of data to inform future decisions: Insights into the ongoing hydrocarbon release at Taylor Energy's Mississippi Canyon Block 20 (MC20) site. *Marine Pollution Bulletin* 155:111056, <https://doi.org/10.1016/j.marpolbul.2020.111056>.
- Burd, A.B., J.P. Chanton, K.L. Daly, S. Gilbert, U. Passow, and A. Quigg. 2020. The science behind marine-oil-snow and MOSSFA: Past, present, and future. *Progress in Oceanography* 187:102398, <https://doi.org/10.1016/j.pocean.2020.102398>.
- Camilli, R., C.M. Reddy, D.R. Yoerger, B.A.S. Van Mooy, M.V. Jakuba, J.C. Kinsey, C.P. McIntyre, S.P. Sylva, and J.V. Maloney. 2010. Tracking hydrocarbon plume transport and biodegradation at Deepwater Horizon. *Science* 330:201–204, <https://doi.org/10.1126/science.1195223>.
- Chanton, J.P., J. Cherrier, R.M. Wilson, J. Sarkodee-Ado, and S. Bosman. 2012. Radiocarbon evidence that carbon from the Deepwater Horizon spill entered the planktonic food web in the Gulf of Mexico. *Environmental Research Letters* 7:045303, <https://doi.org/10.1088/1748-9326/7/4/045303>.
- Chen, H., A. Hou, Y.E. Corilo, Q. Lin, J. Liu, I.A. Mendelsohn, R. Zhuang, R.P. Rogers, and A.M. McKenna. 2016. 4 years after the Deepwater Horizon spill: Molecular transformation of Macondo Well oil in Louisiana salt marsh sediments revealed by FT-ICR mass spectrometry. *Environmental Science & Technology* 50:9,061–9,069, <https://doi.org/10.1021/acs.est.6b01156>.
- Conover, R.J. 1971. Some relationships between zooplankton and bunker C oil in Chedabucto Bay following the wreck of the tanker *Arrow*. *Journal of the Fisheries Research Board of Canada* 29:1,327–1,330, <https://doi.org/10.1139/f71-202>.
- Daly, K., U. Passow, J. Chanton, and D. Hollander. 2016. Assessing the impacts of oil-associated marine snow formation and sedimentation during and after the Deepwater Horizon oil spill. *Anthropocene* 13:18–33, <https://doi.org/10.1016/j.anucene.2016.01.006>.
- Daly, K., A.C. Vaz, and C.B. Paris. 2020. Physical processes influencing the sedimentation and lateral transport of MOSSFA in the NE Gulf of Mexico. Pp. 300–314 in *Scenarios and Responses to Future Deep Oil Spills: Fighting the Next War*. S.A. Murawski, C.H. Ainsworth, S. Gilbert, D.J. Hollander, C.B. Paris, M. Schlüter, and D. Wetzel, eds, Springer Nature, [https://doi.org/10.1007/978-3-030-12963-7\\_18](https://doi.org/10.1007/978-3-030-12963-7_18).
- Dickey, R., and M. Huettel. 2016. Seafood and beach safety in the aftermath of the Deepwater Horizon oil spill. *Oceanography* 29(3):197–203, <https://doi.org/10.5670/oceanog.2016.83>.
- Diercks, A.-R., and V.L. Asper. 1997. *In situ* settling speeds of marine snow aggregates below the mixed layer: Black Sea and Gulf of Mexico. *Deep Sea Research Part I* 44(3):385–398, [https://doi.org/10.1016/S0967-0637\(96\)00104-5](https://doi.org/10.1016/S0967-0637(96)00104-5).
- Diercks, A.-R., R.C. Highsmith, V.L. Asper, D. Joung, Z. Zhou, L. Guo, A.M. Shiller, S.B. Joye, A.P. Teske, N. Guinasso, and others. 2010. Characterization of subsurface polycyclic aromatic hydrocarbons at the Deepwater Horizon Site. *Geophysical Research Letters* 37(20), <https://doi.org/10.1029/2010GL045046>.
- Diercks, A.-R., C. Dike, V.L. Asper, S.F. Dimarco, J.P. Chanton, and U. Passow. 2018. Scales of seafloor sediment resuspension in the northern Gulf of Mexico. *Elementa: Science of the Anthropocene* 6:32, <https://doi.org/10.1525/elementa.285>.
- Douglas, G.D., B. Liu, W. Wong, E. Litman, and J. Hardenstine. 2018. Red crabs as sentinel organisms in exposure of deep-sea benthos to Macondo oil following the Deepwater Horizon oil spill. Pp. 651–681 in *Oil Spill Environmental Forensics Case Studies*. S. Stout and Z. Wang, eds, Butterworth-Heinemann (Elsevier, Oxford, UK), <https://www.sciencedirect.com/science/article/pii/B9780128044346000306>.
- Doyle, S.M., E.A. Whitaker, V. De Pascuale, T.L. Wade, A.H. Knapp, P.H. Santschi, A. Quigg, and J.B. Sylvan. 2018. Rapid formation of microbe-oil aggregates and changes in community composition in coastal surface water following exposure to oil and the dispersant Corexit. *Frontiers in Microbiology* 9:689, <https://doi.org/10.3389/fmicb.2018.00689>.
- Engel, A.S., C. Liu, A.T. Paterson, L.C. Anderson, R.E. Turner, and E.B. Overton. 2017. Salt marsh bacterial communities before and after the Deepwater Horizon oil spill. *Applied and Environmental Microbiology* 83(20):e00784-17, <https://doi.org/10.1128/AEM.00784-17>.
- Farrington, J.W., and H. Takada. 2014. Persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), and plastics: Examples of the status, trend, and cycling of organic chemicals of environmental concern in the ocean. *Oceanography* 27(1):196–213, <https://doi.org/10.5670/oceanog.2014.23>.
- Farrington, J.W., K.A. Burns, and M.S. Leinen. 2016. Synthesis and crosscutting topics of the GoMRI special issue. *Oceanography* 29(3):204–205, <https://doi.org/10.5670/oceanog.2016.84>.
- Farrington, J.W. 2020a. Need to update human health risk assessment protocols for polycyclic aromatic hydrocarbons in seafood after oil spills. *Marine Pollution Bulletin* 150:110744, <https://doi.org/10.1016/j.marpolbul.2019.110744>.
- Farrington, J.W. 2020b. Around Buzzards Bay to a world of ocean science: A personal perspective. *Perspectives of Earth and Space Scientists* 1(1): e2019CN000102, <https://doi.org/10.1029/2019CN000102>.
- Fisher, C.R., P.A. Montagna, and T.T. Sutton. 2016. How did the Deepwater Horizon oil spill impact deep-sea ecosystems. *Oceanography* 29(3):182–195, <https://doi.org/10.5670/oceanog.2016.82>.
- Galstoff, P.S., H.F. Phytcher, R.O. Smith, and V. Koehring. 1935. Effects of crude oil pollution on oysters in Louisiana waters. Pp. 144–208 in *Bulletin of the Bureau of Fisheries*. Volume XLVIII, Bulletin No. 18, Bureau of Fisheries, Department of Commerce, US Government Printing Office, Washington, DC, <https://spo.nmfs.noaa.gov/sites/default/files/pdf-content/fish-bull/fb48.5.pdf>.
- Gearing, J.N., P.J. Gearing, T. Wade, J.G. Quinn, H.B. McCarthy, J. Farrington, and R.F. Lee. 1979. The rates of transport and fates of petroleum hydrocarbons in a controlled marine ecosystem, and a note on analytical variability. *International Oil Spill Conference Proceedings* 1979(1):555–564, <https://doi.org/10.7901/2169-3358-1979-1-555>.
- Giering, S.L.C., B. Yan, J. Sweet, V. Asper, A. Diercks, J.P. Chanton, M. Pitiranggon, and U. Passow. 2018. The ecosystem baseline for particle flux in the Northern Gulf of Mexico. *Elementa: Science of the Anthropocene* 6:6, <https://doi.org/10.1525/elementa.264>.
- Graham, W.M., R.H. Condon, R.H. Carmichael, I. D'Ambr, and H.K. Patterson. 2010. Oil carbon entered the coastal planktonic food web during the Deepwater Horizon oil spill. *Environmental Research Letters* 5:045301, <https://doi.org/10.1088/1748-9326/5/4/045301>.
- Halanych, K.M., C.H. Ainsworth, E.E. Cordes, R.E. Dodge, M. Huettel, I.A. Mendelsohn, S.A. Murawski, C.B. Paris-Limouzy, P.T. Schwing, R.F. Shaw, and T. Sutton. 2021. Effects of petroleum by-products and dispersants on ecosystems. *Oceanography* 34(1):152–163, <https://doi.org/10.5670/oceanog.2021.123>.
- Hayworth, J.S., T.P. Clement, G.F. John, and F. Yin. 2015. Fate of Deepwater Horizon oil in Alabama's beach system: Understanding the physical evolution processes based on observational data. *Marine Pollution Bulletin* 90:95–105, <https://doi.org/10.1016/j.marpolbul.2014.11.016>.
- Huettel, M., W.A. Overholt, J.E. Kostka, C. Hagan, J. Kaba, W.B. Wells, and S. Dudley. 2018. Degradation of Deepwater Horizon oil buried in a Florida beach influenced by tidal pumping. *Marine Pollution Bulletin* 126:488–500, <https://doi.org/10.1016/j.marpolbul.2017.10.061>.
- Iqbal, J., R.J. Portier, and D. Giscclair. 2007. Aspects of petrochemical pollution in coastal Louisiana, USA. *Marine Pollution Bulletin* 54:792–819, <https://doi.org/10.1016/j.marpolbul.2007.02.004>.
- Ji, C., C.J. Beegle-Krauss, and J.D. Englehardt. 2020. Formation, detection, and modeling of submerged oil: A review. *Journal of Marine Science and Engineering* 8:642, <https://doi.org/10.3390/jmse8090642>.
- Johansson, S., U. Larson, and P. Boehm. 1980. The Tsesis oil spill: Impacts on the pelagic ecosystem. *Marine Pollution Bulletin* 11:284–291, [https://doi.org/10.1016/0025-326X\(80\)90166-6](https://doi.org/10.1016/0025-326X(80)90166-6).
- John, G.F., Y. Han, and T.P. Clement. 2016. Weathering patterns of polycyclic aromatic hydrocarbons contained in submerged Deepwater Horizon oil residues when re-exposed to sunlight. *Science of the Total Environment* 573:189–202, <https://doi.org/10.1016/j.scitotenv.2016.08.059>.
- Kennicutt, M.C. 2017. Oil and gas seeps in the Gulf of Mexico. Pp. 275–358 in *Habitats and Biota of the Gulf of Mexico: Before the Deepwater Horizon Oil Spill*. C. Ward, ed., Springer, New York, NY, [https://doi.org/10.1007/978-1-4939-3447-8\\_5](https://doi.org/10.1007/978-1-4939-3447-8_5).
- Kirman, Z.D., J.L. Sericano, T.L. Wade, T.S. Bianchi, F. Marcantonio, and A.S. Kolker. 2016. Composition and depth distribution of hydrocarbons in Barataria Bay marsh sediments after the Deepwater Horizon oil spill. *Environmental Pollution* 214:101–113, <https://doi.org/10.1016/j.envpol.2016.03.071>.
- Kolpack, R.L., ed. 1971. *Biological and Oceanographical Survey of the Santa Barbara Channel Oil Spill, 1969–1970, Vol. II. Physical, Chemical, and Geological Studies*. Alan Hancock Foundation, University of Southern California, Los Angeles, CA, 477 pp.
- Kostka, J., S. Joye, and R. Colwell. 2020. Deepwater Horizon and the rise of omics. *Eos* 101:28–33, <https://doi.org/10.1029/2020EO140140>.
- Kujawinski, E.B., C.M. Reddy, R.P. Rogers, J.C. Thrash, D.L. Valentine, and H.K. White. 2020. The first decade of scientific insights from the Deepwater Horizon oil release. *Nature Reviews Earth and Environment* 1:237–250, <https://doi.org/10.1038/s43017-020-0046-x>.
- Lea-Smith, D.J., S.J. Biller, M.P. Davey, C.A.R. Cotton, B.M. Perez Sepulveda, A.V. Turchyn, D.J. Scanlan, A.G. Smith, S.W. Chisholm, and C.J. Howe. 2015. Contribution of cyanobacterial alkane production to the ocean hydrocarbon cycle. *Proceedings of the*



- National Academy of Sciences of the United States of America 112(44):13,591–13,596, <https://doi.org/10.1073/pnas.1507274112>.
- Ledwell, J.R., R. He, Z. Xue, S.F. Dimarco, L.J. Spencer, and P. Chapman. 2016. Dispersion of a tracer in the deep Gulf of Mexico. *Journal of Geophysical Research: Oceans* 121:1,110–1,132, <https://doi.org/10.1002/2015JC011405>.
- Lee, R.F., M. Köster, and G.A. Paffenhöfer. 2012. Ingestion and defecation of dispersed oil droplets by pelagic tunicates. *Journal of Plankton Research* 34(12):1,058–1,063, <https://doi.org/10.1093/plankt/fbs065>.
- Lee, K., M. Boufadel, B. Chen, J. Foght, P. Hodson, S. Swanson, and A. Venosa. 2015. *Expert Panel Report on the Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments*. Royal Society of Canada, Ottawa, ON, 461 pp.
- Lima, A.L.C., J.W. Farrington, and C.R. Reddy. 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—A review. *Environmental Forensics* 6:109–131, <https://doi.org/10.1080/15275920509052739>.
- Lin, Q., I.A. Mendelsohn, S.A. Graham, A. Hou, J.W. Fleeger, and D.R. Deis. 2016. Response of salt marshes to oiling from the Deepwater Horizon spill: Implications for plant growth, soil surface erosion, and shoreline stability. *Science of the Total Environment* 557–558:369–377, <https://doi.org/10.1016/j.scitotenv.2016.03.049>.
- Liu, G., A. Bracco, and U. Passow. 2018. The influence of mesoscale and submesoscale circulation on sinking particles in the Northern Gulf of Mexico. *Elementa: Science of the Anthropocene* 6:36, <https://doi.org/10.1525/elementa.292>.
- MacDonald, I.R., O. Garcia-Pineda, A. Beet, S. Dangesgar Asi, L. Feng, G. Grattinger, D. French-MacKay, J. Holmes, C. Hu, F. Huffer, and others. 2015. Natural and unnatural oil slicks in the Gulf of Mexico. *Journal of Geophysical Research: Oceans* 120(12):8,364–8,380, <https://doi.org/10.1002/2015JC011062>.
- MacKay, D., W.Y. Shiu, and M.C. Ma. 1992. *Illustrated Handbook of Physical Chemical Properties and Environmental Fate of Organic Chemicals (Vol. 1 Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs; Vol. II Polynuclear Aromatics Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans)*. Lewis Publishers, Boca Raton, FL USA.
- McNutt, M.K., S. Chu, J. Lubchenko, T. Hunter, G. Dreyfus, S.A. Murawski, and D.M. Kennedy. 2012. Applications of science and engineering to quantify and control the Deepwater Horizon oil spill. *Proceedings of the National Academy of Sciences of the United States of America* 109:20,222–20,228, <https://doi.org/10.1073/pnas.1214389109>.
- Meyer, B.M., P.L. Adhikari, G.M. Olson, M.S. Miles, and E.B. Overton. 2018. Louisiana coastal marsh environments and MC252 oil biomarker chemistry. Pp. 737–756 in *Oil Spill Environmental Forensics Case Studies*. Z. Wang, and S.A. Stout, eds, Elsevier, <https://doi.org/10.1016/B978-0-12-804434-6.00032-X>.
- Michel, J., E.H. Owens, S. Zengel, A. Graham, Z. Nixon, T. Allard, W. Holton, P.D. Reimer, A. Lamarches, M. White, and others. 2013. Extent and degree of shoreline oiling: Deepwater Horizon oil spill, Gulf of Mexico, USA. *PLoS ONE* 8(6):e65087, <https://doi.org/10.1371/journal.pone.0065087>.
- Mitchellmore, C.A., A.C. Bejarano, and D.L. Wetzel. 2020. A synthesis of DWH oil: Chemical dispersant and chemically dispersed oil aquatic standard acute and chronic toxicity studies. 2020. Pp. 480–496 in *Deep Oil Spills: Facts, Fate, and Effects*. S.A. Murawski, C.H. Ainsworth, S. Gilbert, D.J. Hollander, C.B. Paris, M. Schlüter, and D.L. Wetzel, eds, Springer Nature, [https://doi.org/10.1007/978-3-030-11605-7\\_28](https://doi.org/10.1007/978-3-030-11605-7_28).
- Mitra, S., D.G. Kimmel, J. Snyder, K. Scalise, B.D. McLaughon, M.R. Roman, G.J. John, J.J. Pierson, S.B. Brandt, J.P. Montoya, and others. 2012. Macondo-1 well oil-derived polycyclic aromatic hydrocarbons in mesozooplankton from the northern Gulf of Mexico. *Geophysical Research Letters* 39(1), <https://doi.org/10.1029/2011GL049505>.
- Murawski, S.A., W.T. Hogarth, E.B. Peebles, and L. Barbieri. 2014. Prevalence of external skin lesions and polycyclic aromatic hydrocarbon concentrations in Gulf of Mexico fishes post-Deepwater Horizon. *Transactions of the American Fisheries Society* 143:1,084–1,097, <https://doi.org/10.1080/00028487.2014.911205>.
- Murawski, S.A., M. Grosell, C. Smith, T. Sutton, K.M. Halanych, R.F. Shaw, and C.A. Wilson. 2021. Impacts of petroleum, petroleum components, and dispersants on organisms and populations. *Oceanography* 34(1):136–151, <https://doi.org/10.5670/oceanog.2021.122>.
- NASEM (National Academy of Sciences, Engineering, and Medicine). 2020. *The Use of Dispersants in Marine Oil Spill Responses*. The National Academies Press, Washington, DC, 340 pp., <https://doi.org/10.17226/25161>.
- NRC (National Research Council). 1975. *Petroleum in the Marine Environment*. National Academies Press, Washington, DC, 107 pp.
- NRC. 1985. *Oil in the Sea: Inputs, Fates, and Effects*. National Academies Press, Washington, DC, 601 pp.
- NRC. 1993. *Assessment of the US Outer Continental Shelf Environmental Studies Program: IV. Lessons and Opportunities*. National Academies Press, Washington, DC, 59 pp.
- NRC. 1999. *Spills of Non-Floating Oils: Risk and Response*. National Academy Press, Washington, DC, 88 pp., <https://doi.org/10.17226/9640>.
- Passow, U., and R.D. Hetland. 2016. What happened to all the oil? *Oceanography* 29(3):88–95, <https://doi.org/10.5670/oceanog.2016.73>.
- Passow, U., and K. Ziervogel. 2016. Marine snow sedimented oil released during the Deepwater Horizon spill. *Oceanography* 29(3):118–125, <https://doi.org/10.5670/oceanog.2016.76>.
- Passow, U., and S.A. Stout. 2020. Character and sedimentation of “lingering” Macondo oil to the deep-sea after the Deepwater Horizon oil spill. *Marine Chemistry* 218:103733, <https://doi.org/10.1016/j.marchem.2019.103733>.
- Passow, U., and E.B. Overton. 2021. The complexity of spills: The fate of the Deepwater Horizon oil. *Annual Reviews of Marine Science* 13:109–136, <https://doi.org/10.1146/annurev-marine-032320-095153>.
- Payne, J.R., and C.R. Philipps. 1985. Photochemistry of petroleum in water. *Journal of Environmental Science and Technology* 19(7):569–579, <https://doi.org/10.1021/es00137a602>.
- Payne, J.R., and W.B. Driskell. 2018. Macondo oil in northern Gulf of Mexico waters: Part 1. Assessment and forensic methods for Deepwater Horizon offshore water samples. *Marine Pollution Bulletin* 129:399–411, <https://doi.org/10.1016/j.marpolbul.2018.02.055>.
- Pine, C. 2006. Hurricane Katrina and oil spills: Impact on coastal and ocean environments. *Oceanography* 19(2):37–39, <https://doi.org/10.5670/oceanog.2006.61>.
- Quigg, A., U. Passow, W.-C. Chin, L. Bretherton, M. Kamalanathan, C. Xu, K.A. Schwehr, S. Zhang, L. Sun, T.L. Wade, and others. 2016. The role of microbial exopolymers in determining the fate of oil and chemical dispersants in the ocean. *Limnology and Oceanography Letters* 1:3–26, <https://doi.org/10.1002/lol2.10030>.
- Quigg, A., U. Passow, K.L. Daly, A. Burd, D.J. Hollander, P.T. Schwing, and K. Lee. 2020. Marine oil snow sedimentation and flocculent accumulations (MOSSFA) events: Learning from the past to predict the future. Pp. 196–234 in *Deep Oil Spills: Facts, Fates, and Effects*. S.A. Murawski, C.H. Ainsworth, S. Gilbert, D.J. Hollander, C.B. Paris, M. Schlüter, and D.L. Wetzel, eds, Springer Nature, [https://doi.org/10.1007/978-3-030-11605-7\\_12](https://doi.org/10.1007/978-3-030-11605-7_12).
- Quigg, A., J.W. Farrington, S. Gilbert, S.A. Murawski, and V.T. John. 2021. A decade of GoMRI dispersant science: Lessons learned and recommendations for the future. *Oceanography* 34(1):98–111, <https://doi.org/10.5670/oceanog.2021.119>.
- Quintana-Rizzo, E., J.J. Torres, S.W. Ross, I. Romero, K. Watson, E. Goddard, and D. Hollander. 2015.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in deep-living fishes and shrimps after the Deepwater Horizon oil spill. *Marine Pollution Bulletin* 94(1–2):241–250, <https://doi.org/10.1016/j.marpolbul.2015.02.002>.
- Reeburgh, W.S. 2007. Oceanic methane biogeochemistry. *Chemical Reviews* 107:486–513, <https://doi.org/10.1021/cr050362v>.
- Remsen, A., T.L. Hopkins, and S. Samson. 2004. What you see is not what you catch: A comparison of concurrently collected net, Optical Plankton Counter, and Shadowed Image Particle Profiling Evaluation Recorder data from the northeast Gulf of Mexico. *Deep Sea Research Part I* 51:129–151, <https://doi.org/10.1016/j.dsr.2003.09.008>.
- Romero, I.C., P.T. Schwing, G.R. Brooks, R.A. Larson, D.W. Hastings, G. Ellis, E.A. Goddard, and D.H. Hollander. 2015. Hydrocarbons in deep-sea sediments following the 2010 Deepwater Horizon blowout in the northeast Gulf of Mexico. *PLoS ONE* 10(5):e0128371, <https://doi.org/10.1371/journal.pone.0128371>.
- Romero, I.C., G. Toro-Farmer, A.-R. Diercks, P. Schwing, F. Mueller-Karger, S. Murawski, and D.J. Hollander. 2017. Large-scale deposition of weathered oil in the Gulf of Mexico following a deep-water oil spill. *Environmental Pollution* 228:179–189, <https://doi.org/10.1016/j.envpol.2017.05.019>.
- Romero, I.C., H. Juddkins, and M. Vecchione. 2020. Temporal variability of polycyclic aromatic hydrocarbons in deep-sea cephalopods in the Northern Gulf of Mexico. *Frontiers in Marine Science* 7:54, <https://doi.org/10.3389/fmars.2020.00264>.
- Rowe, G.T., and M.C. Kennicutt. 2008. Introduction to the Deep Gulf of Mexico Benthos Program. *Deep Sea Research Part II* 55:2,536–2,540, <https://doi.org/10.1016/j.dsr2.2008.09.002>.
- Royal Society. 1980. *The Effects of Oil Pollution: Some Research Needs*. The Royal Society, London, UK, 103+ pp.
- Rullkötter, J., and J.W. Farrington. 2021. What was released? Assessing the physical properties and chemical composition of petroleum and products of burned oil. *Oceanography* 34(1):44–57, <https://doi.org/10.5670/oceanog.2021.116>.
- Sandifer, P.A., A. Ferguson, M.L. Finucane, M. Partyka, H.M. Solo-Gabriele, A.H. Walker, K. Wowk, R. Caffey, and D. Yoskowitz. 2021. Human health and socioeconomic effects of the Deepwater Horizon oil spill in the Gulf of Mexico. *Oceanography* 34(1):174–191, <https://doi.org/10.5670/oceanog.2021.125>.
- Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden. 2017. *Environmental Organic Chemistry, Third Edition*. John Wiley & Sons, Hoboken, NJ, 1,005 pp.
- Silver, M. 2015. Marine snow: A brief historical sketch. *Limnology and Oceanography Bulletin* 24(1):5–10, <https://doi.org/10.1002/lob.10005>.
- Snyder, S.M., E.I. Pulser, D.L. Wetzel, and S.A. Murawski. 2015. PAH exposure in Gulf of Mexico demersal fishes, post-Deepwater Horizon. *Environmental Science & Technology* 49:8,786–8,795, <https://doi.org/10.1021/acs.est.5b01870>.
- Socolofsky, S.A., E.E. Adams, C.B. Paris, and D.Y. Yang. 2016. How do oil, gas, and water interact near a subsea blowout? *Oceanography* 29(3):64–75, <https://doi.org/10.5670/oceanog.2016.63>.
- Soliman, Y.S., and T.L. Wade. 2008. Estimates of PAHs burdens in a population of ampeliscid amphipods at the head of Mississippi Canyon (N. Gulf of Mexico). *Deep Sea Research Part II* 55:2,577–2,584, <https://doi.org/10.1016/j.dsr2.2008.07.007>.

- Steen, A.D., S. Kusch, H.A. Abdullah, N. Cakić, S. Coffinet, T. Dittmar, J.M. Fulton, V. Galy, K.-U. Hinrichs, A.E. Ingalls, and others. 2020. Analytical and computational advances, opportunities, and challenges in marine organic biogeochemistry in an era of “omics.” *Frontiers in Marine Science* 7:718, <https://doi.org/10.3389/fmars.2020.00718>.
- Stout, S.A., and J.R. Payne. 2016a. Macondo oil in deep-sea sediments: Part 1. Sub-sea weathering of oil deposited on the seafloor. *Marine Pollution Bulletin* 111:365–380, <https://doi.org/10.1016/j.marpolbul.2016.07.036>.
- Stout, S.A., and J.R. Payne. 2016b. Chemical composition of floating and sunken in-situ burn residues from the Deepwater Horizon spill. *Marine Pollution Bulletin* 108:186–202, <https://doi.org/10.1016/j.marpolbul.2016.04.031>.
- Stout, S.A., J.R. Payne, R.W. Ricker, G. Baker, and C. Lewis. 2016. Macondo oil in deep sea sediments: Part 2. Distribution and distinction from background and natural oil seeps. *Marine Pollution Bulletin* 111:381–401, <https://doi.org/10.1016/j.marpolbul.2016.07.041>.
- Stout, S.A., and J.R. Payne. 2017. Footprint, weathering and persistence of synthetic-base drilling mud olefins in deep-sea sediments following the Deepwater Horizon disaster. *Marine Pollution Bulletin* 118:328–340, <https://doi.org/10.1016/j.marpolbul.2017.03.013>.
- Stout, S.A., and Z. Wang, eds. 2018. *Oil Spill Environmental Forensics Case Studies*. Butterworth-Heinemann/Elsevier, Cambridge, MA, 843 pp.
- Takada, H., and H.K. Karapangioti, eds. 2019. *Hazardous Chemicals Associated with Plastics in the Marine Environment*. D. Barceló and A.G. Kostianoy, eds, The Handbook of Environmental Chemistry, vol. 78. Springer, 315 pp., <https://doi.org/10.1007/978-3-319-95568-1>.
- Tarr, M., P. Zito, E.B. Overton, G.M. Olson, P.L. Adhikari, and C.M. Reddy. 2016. Weathering of oil spilled in the marine environment. *Oceanography* 29(3):126–135, <https://doi.org/10.5670/oceanog.2016.77>.
- Tatarivu, C., N. Flournoy, A.A. Kleinhuizen, D. Tolle, E.B. Overton, P. Sobczyk, and B. Mortazavi. 2018. Salt marsh denitrification is impacted by oiling intensity six years after the Deepwater Horizon oil spill. *Environmental Pollution* 243(Part B):1606–1614, <https://doi.org/10.1016/j.envpol.2018.09.034>.
- Transportation Research Board and National Research Council. 2003. *Oil in the Sea III: Inputs, Fates and Effects*. National Academies Press, Washington, DC, 265 pp., <https://doi.org/10.17226/10388>.
- Turner, R.E., N.N. Rabalais, E.B. Overton, B.M. Meyer, G. McClenachan, E.M. Swenson, M. Besonen, M.L. Parsons, and J. Zingre. 2019. Oiling of the continental shelf and coastal marshes over eight years after the 2010 Deepwater Horizon oil spill. *Environmental Pollution* 252:1367–1376, <https://doi.org/10.1016/j.envpol.2019.05.134>.
- Valentine, D.L., and C.M. Reddy. 2015. Latent hydrocarbons from cyanobacteria. (Commentary). *Proceedings of the National Academy of Sciences of the United States of America* 112(44):13,434–13,435, <https://doi.org/10.1073/pnas.1518485112>.
- Wade, T.L., Y. Soliman, S.T. Sweet, G.A. Wolff, and B.J. Presley. 2008. Trace elements and polycyclic aromatic hydrocarbons (PAHs) concentrations in deep Gulf of Mexico sediments. *Deep Sea Research Part II* 55:2,585–2,593, <https://doi.org/10.1016/j.dsr2.2008.07.006>.
- Wakeham, S.G., and E.A. Canuel. 2016. Biogenic polycyclic aromatic hydrocarbons in sediment of the San Joaquin River in California (USA), and current paradigms on their formation. *Environmental Science and Pollution Research* 23:10,426–10,442, <https://doi.org/10.1007/s11356-015-5402-x>.
- Wakeham, S.G., and C. Lee. 2019. Limits of our knowledge: Part 2. Selected frontiers in marine organic biogeochemistry. *Marine Chemistry* 212:16–46, <https://doi.org/10.1016/j.marchem.2019.02.005>.
- Ward, C.P., C.J. Armstrong, R.N. Conmy, D.P. French-McCay, and C.M. Reddy. 2018. Photochemical oxidation of oil reduced the effectiveness of aerial dispersants applied in response to the Deepwater Horizon spill. *Environmental Science & Technology Letters* 5(5):226–231, <https://doi.org/10.1021/acs.estlett.8b00084>.
- Ward, C.P., and E.B. Overton. 2020. How the 2010 Deepwater Horizon spill reshaped our understanding of crude oil photochemical weathering at sea: A past, present, and future perspective. *Environmental Science: Processes & Impacts* 22:1,125–1,138, <https://doi.org/10.1039/D0EM00027B>.
- Ward, C.P., C.M. Reddy, and E.B. Overton. 2020. Why sunlight matters for marine oil spills. *Eos* 101, <https://doi.org/10.1029/2020EO143427>.
- Watson, K., I. Romero, S. Murawski, and D.J. Hollander. 2013. Large-scale tracking of oil-derived hydrocarbons after the Deepwater Horizon blowout: Reconstructing spatial and temporal petroleum distribution. Paper presented at the Gulf of Mexico Oil Spill & Ecosystem Science Conference 2013, New Orleans, LA, January 21–23, 2013.
- Watson, K. 2014. *Spatial and Temporal Extent of a Subsurface Hydrocarbon Intrusion Following the Deepwater Horizon Blowout*. MS Thesis, College of Marine Science, University of South Florida, 61 pp.
- Weiman, S., S.B. Joye, J.E. Kostka, K.M. Halanaych, and R.R. Colwell. 2021. GoMRI insights into microbial genomics and hydrocarbon bioremediation response in marine ecosystems. *Oceanography* 34(1):124–135, <https://doi.org/10.5670/oceanog.2021.121>.
- Westerholm, D.G., C.H. Ainsworth, C.H. Barker, P.G. Brewer, J.W. Farrington, D. Justić, V.H. Kourafalou, S.A. Murawski, J.G. Shepherd, and H.M. Solo-Gabriele. 2021. Preparedness, planning, and advances in operational response. *Oceanography* 34(1):212–227, <https://doi.org/10.5670/oceanog.2021.120>.
- White, H.H., P.Y. Hsing, W. Cho, T.M. Shank, E.E. Cordes, A.M. Quatrini, R.K. Nelson, R. Camilli, A.W. Demopolous, and C.R. German. 2012. Impact of Deepwater Horizon oil spill on a deep water coral community in the Gulf of Mexico. *Proceedings of the National Academy of Sciences of the United States of America* 109(50):20,303–20,308, <https://doi.org/10.1073/pnas.1118029109>.
- White, H.K., C.H. Wang, P.L. Williams, D.M. Findley, A.M. Thurston, C. Aepppli, R.K. Nelson, and C.M. Reddy. 2016. Long-term weathering and continued oxidation of oil residues from the Deepwater Horizon spill. *Marine Pollution Bulletin* 113:380–386, <https://doi.org/10.1016/j.marpolbul.2016.10.029>.
- Wilson, R.M., J. Cherrier, J. Sarkodee-Adoo, S. Bosman, A. Mickle, and J.P. Chanton. 2016. Tracing the intrusion of fossil carbon into coastal Louisiana macrofauna using natural <sup>14</sup>C and <sup>13</sup>C abundances. *Deep Sea Research Part II* 129:89–95, <https://doi.org/10.1016/j.dsr2.2015.05.014>.
- Yan, B., U. Passow, J.P. Chanton, E.-M. Nöthig, V. Asper, J. Sweet, M. Pitiranggon, A. Diercks, and D. Pak. 2016. Sustained deposition of contaminants from the Deepwater Horizon spill. *Proceedings of the National Academy of Sciences of the United States of America* 113(24): E3332–E3340, <https://doi.org/10.1073/pnas.1513156113>.
- Ylitalo, G.M., M.M. Krahn, W.W. Dickoff, J. Stein, W.W. Walker, C.L. Lassiter, E.S. Garrett, L.S. Desfosse, K.M. Itchell, B.T. Noble, and others. 2012. Federal seafood safety response to the Deepwater Horizon oil spill. *Proceedings of the National Academy of Sciences of the United States of America* 109(50):20,274–20,279, <https://doi.org/10.1073/pnas.110886109>.
- Zimmermann, L.A., M.G. Feldman, D.S. Benoit, M.J. Carron, N.M. Dannreuther, K.H. Fillingham, J.C. Gibeau, J.L. Pettit, J.B. Ritchie, R.R. Rossi, and others. 2021. From disaster to understanding: Formation and accomplishments of the Gulf of Mexico Research Initiative. *Oceanography* 34(1):16–29, <https://doi.org/10.5670/oceanog.2021.114>.

## ACKNOWLEDGMENTS

We thank Margaret Leinen and Peter Brewer of the GoMRI Research Board for providing early guidance for the content of this paper. We acknowledge the efforts of several hundred researchers within the Gulf of Mexico Research Initiative, the BP- and US government-funded DWH Natural Resource Damage Assessment efforts, the US National Science Foundation Rapid Response Program, NOAA Sea Grant, and several other sources of funding too numerous to mention that contributed to advancing knowledge of the fates of gas and oil inputs from the DWH accident. Adrian Burd, Joel Koska, Elizabeth Kujawinski, Samantha Joye, Antonietta Quigg, and Collin Ward co-lead GoMRI synthesis workshops and/or were lead authors of recent papers reviewing key aspects of biogeochemical fates of DWH inputs. We thank GoMRI “fates” workshop participants Puspa Adhikari, Chris Barker, Michel Boufadel, Edward Buskey, Tom Coolbaugh, Emily Maugh-Douglas, the late David Hollander, Charlie Henry, Vijay John, Zanfei Liu, Jim Payne, Isabel Romero, Dalina Thrift-Viverous, Terry Wade, and Stephen Wise for sharing their knowledge. John Shepherd and Richard Shaw ably coordinated the overall synthesis effort. Charles Wilson, Chief Scientific Officer of GoMRI; Michael Carron and Kevin Shaw of the GoMRI Management Team; Michael Feldman and Callan Yanoff and colleagues at the Consortium for Ocean Leadership; and Jennifer Pettit of the American Institute of Biological Sciences provided excellent administrative support for the GoMRI synthesis efforts. Three peer reviewers provided helpful comments that strengthened the manuscript. Edward Overton thanks GoMRI for financial support for this review, and Uta Passow thanks GoMRI and the Multi-Partner Research Initiative under Canada’s Ocean Protection Plan for funding her participation in this review. John Farrington is a member of the GoMRI Research Board.

## AUTHORS

**John W. Farrington** (jfarrington@whoi.edu) is Dean Emeritus, Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA, USA. **Edward B. Overton** is Professor Emeritus, Department of Environmental Sciences, Louisiana State University, Baton Rouge, LA, USA. **Uta Passow** is Canada Research Chair in Biological Oceanographic Processes, Ocean Sciences Centre, Memorial University, St John’s, NL, Canada.

## ARTICLE CITATION

Farrington, J.W., E.B. Overton, and U. Passow. 2021. Biogeochemical processes affecting the fate of discharged Deepwater Horizon gas and oil: New insights and remaining gaps in our understanding. *Oceanography* 34(1):76–97, <https://doi.org/10.5670/oceanog.2021.118>.

## COPYRIGHT & USAGE

This is an open access article made available under the terms of the Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution, and reproduction in any medium or format as long as users cite the materials appropriately, provide a link to the Creative Commons license, and indicate the changes that were made to the original content.